UNIVERSITAT DE VALÈNCIA

Departamento de Medicina Preventiva y Salud Pública, Bromatología, Toxicología y Medicina Legal

Influencia de la composición en las propiedades físicas y sensoriales de postres lácteos semisólidos

TESIS DOCTORAL

Presentada por:
Mª Amparo Tárrega Guillem

Dirigida por:
Dra. Elvira Costell Ibáñez

Valencia, Julio 2005

Instituto de Agroquímica y Tecnología de Alimentos

CSIC

Laboratorio de Propiedades Físicas y Sensoriales

MINISTERIO
DE EDUCACION
Y CIENCIA

CONSEJO SUPERIOR
DE INVESTIGACIONES
CIENTÍFICAS
INSTITUTO DE AGROQUÍMICA
Y TECNOLOGÍA DE ALIMENTOS

Dª Elvira Costell Ibáñez, Profesora de Investigación del Instituto de Agroquímica y Tecnología de Alimentos del Consejo Superior de Investigaciones Científicas

Hace constar:

Que la memoria titulada **"INFLUENCIA DE LA COMPOSICIÓN EN LAS PROPIEDADES FÍSICAS Y SENSORIALES DE POSTRES LÁCTEOS SEMISÓLIDOS"** presentada por Dª Mª Amparo Tárrega Guillem para optar al grado de Doctor por la Universidad de Valencia, ha sido realizada en el Instituto de Agroquímica y Tecnología de Alimentos (CSIC) bajo su dirección y que reúne las condiciones necesarias para ser defendida por su autora.

Paterna, 5 de julio de 2005

Fdo.: Dra. Elvira Costell Ibáñez

Direc. Postal: APARTADO CORREOS, 73
46100 BURJASSOT (VALENCIA)
Domicilio Social: POLÍGONO LA COMA, S/N
46980 PATERNA (VALENCIA)
TEL: +34 96 390 00 22
FAX: +34 96 363 63 01
Sitio Web: http://www.iata.csic.es

A mi madre, mi fuerza

Ante todo, deseo expresar mi agradecimiento a Elvira Costell que durante estos cuatro años ha querido enseñarme, motivarme, apoyarme y potenciarme de forma admirable e incansable. Sinceramente me gustaría que supiera lo afortunada que me siento de que haya sido mi directora de tesis.

También quiero expresar mi agradecimiento a mis muy queridos Luis Durán y Luis Izquierdo que de forma muy especial han colaborado en este mismo empeño.

Gracias a Mª Jesús Hernández, Manolo Dolz y al Profesor Rao por compartir conmigo sus conocimientos sobre reología.

Gracias a mis compañeros Inma, Sara, Edith, Mª Luisa, Beatriz, Piyada, Jorge y en especial a Luis por su ayuda en mi trabajo. A ellos y también a Reme, Leire, Teresa, Ana, Raquel, Susana, Paula, Miguel Ángel, Tomás, Moisés y David, gracias por los buenos ratos que hemos pasado.

Al Instituto de Agroquímica y Tecnología de Alimentos y al Ministerio de Ciencia y Tecnología, por aportar los recursos necesarios para llevar a cabo esta investigación.

De forma especial quiero agradecer el apoyo de mi familia. A mis hermanas Consuelo y Ana por ayudarme siempre. A Consuelo y Francisco por ser la combinación perfecta de padres.... por todo lo que soy.

A Sergio, por su comprensión, su cariño y su amor.

ÍNDICE GENERAL

INTRODUCCIÓN GENERAL 1

OBJETIVOS 15

PRESENTACIÓN DE LOS TRABAJOS Y JUSTIFICACIÓN DE LA UNIDAD TEMÁTICA 19

CAPÍTULO 1: ***Flow behaviour of semi-solid dairy desserts. Effect of temperature*** 25

1. Introduction 28
2. Materials and methods 30
   - 2.1. Materials 30
   - 2.2. Methods 31
     - 2.2.1. Soluble solids and pH 31
     - 2.2.2. Rheological measurements 31
       - 2.2.2.1. Time dependence 31
       - 2.2.2.2. Flow behaviour 33
   - 2.3. Statistical analysis 34
3. Results and discussion 34
   - 3.1. Influence of temperature on flow time dependence 34
     - 3.1.1. Hysteresis area 34
     - 3.1.2. Shear stress decay test 37
   - 3.2. Influence of temperature on steady flow behaviour 43

References 46

CAPÍTULO 2: ***Rheological characterization of semi-solid dairy desserts. Effect of temperature*** 51

1. Introduction 54
2. Materials and methods 56
   - 2.1. Samples 56
   - 2.2. Rheological measurements 57
     - 2.2.1. Steady shear data 57

2.2.2. Small amplitude oscillatory shear data 58
2.3. Statistical analysis.....58
3. Results 59
3.1. Steady shear data 59
3.2. Dynamic rheological data 61
3.3. Cox–Merz rule 65
References 67

CAPÍTULO 3: ***Colour and consistency of semi-solid dairy desserts. Instrumental and sensory measurements.*** 71

1. Introduction 74
2. Materials and methods.....76
2.1. Samples.....76
2.2. Color measurements 77
2.3. Rheological measurements 77
2.4. Sensory evaluation.....78
2.4. Statistical analysis.....79
3. Results 79
3.1. Instrumental measurements 79
3.1.1. Colour.....79
3.1.2. Rheology.....82
3.2. Sensory analysis.....85
3.3. Relationship between instrumental and sensory data 87
References 88

CAPÍTULO 4: ***Vane yield stress of native and cross-linked starch dispersions in skim milk. Effects of starch concentration and l-carrageenan addition.*** 93

1. Introduction 96
2. Materials and methods.....99
2.1. Materials 99
2.2. Sample preparation 99
2.3. Rheological measurements 100
2.4. Statistical analysis.....100

3. Results 101
3.1. Shear stress-time curves 101
3.2. Effect of starch concentration on $\sigma_{0\text{-}S}$ and $\sigma_{0\text{-}D}$ values 103
3.3. Effect of carrageenan concentration on $\sigma_{0\text{-}S}$ and $\sigma_{0\text{-}D}$ values 106
3.4. Texture map 110
4. Conclusions 111
References 112

CAPÍTULO 5: ***Influence of milk on the rheological behaviour of crosslinked waxy maize and tapioca starch dispersions.*** 117

1. Introduction 120
2. Materials and methods.....122
2.1. Materials 122
2.2. Starch pasting procedure.....122
2.3. Rheological measurements 123
2.3.1. Flow behaviour 124
2.3.2. Viscoelastic properties.....124
2.4. Statistical analysis.....125
3. Results 125
3.1. Viscosity–temperature profiles 125
3.2. Flow behaviour 130
3.3. Viscoelastic properties.....136
References 140

CAPÍTULO 6: ***Effect of composition on the viscoelastic behaviour and on sensory properties of semisolid dairy desserts*** 145

1. Introduction 148
2. Materials and methods.....150
2.1. Materials 150
2.2. Viscosity profile during thermomechanical process.....150
2.3. Rheological measurements 151
2.4. Sensory analysis.....152
2.5. Statistical analysis.....153

3. Results 153
3.1. Viscosity-temperature profiles.....153
3.2. Viscoelastic properties.....156
3.3. Sensory evaluation.....162
References 166

CAPÍTULO 7: ***Effect of inulin addition on rheological and sensory properties of fat free starch based dairy desserts*** 171

1. Introduction 174
2. Materials and methods.....176
2.1. Materials 176
2.2. Viscosity profile during thermomechanical process.....176
2.3. Rheological measurements 177
2.4. Sensory analysis.....178
2.5. Statistical analysis.....179
3. Results 180
3.1. Viscosity-temperature profiles.....180
3.2. Flow behaviour 183
3.3. Viscoelastic properties.....187
3.4. Sensory evaluation.....190
4. Conclusions 193
References 193

RESUMEN Y DISCUSIÓN DE LOS RESULTADOS 199

CONCLUSIONES.....211

INTRODUCCIÓN GENERAL

El concepto tradicional de nutrición, según el cual el objetivo principal de la alimentación es aportar suficientes nutrientes para satisfacer los requerimientos metabólicos de los individuos proporcionándoles una nutrición adecuada, ha evolucionado, por lo menos en los países industrializados, hacia el concepto de "nutrición óptima". Ello ha dado lugar a la aparición de una nueva gama de alimentos y productos que, además de nutrir, mejoran la salud incrementando el bienestar y reduciendo el riesgo de contraer determinadas enfermedades. Respondiendo a este concepto, se han propuesto diferentes términos, de significado más o menos amplio, para denominarlos: saludables (Bello, 2001), funcionales (Hasler, 1998 y 2000), medicinales (IFT, 1992), nutraceúticos (Dillard y German, 2000; Andlauer y Furst, 2002), probióticos, prebióticos y simbióticos (Madley, 2001; Holzapfel y Schillinger, 2002). Aunque hay una cierta controversia sobre el significado de algunos de ellos, actualmente, parece que existe un acuerdo en separar lo que son productos o suplementos dietéticos (nutracéuticos) (Zeisel,1999) de los alimentos que tienen unas características o componentes especiales pero que se consumen como parte de la dieta habitual (funcionales). En el documento consensuado publicado como resultado de la acción concertada europea "Functional Food Science in Europe (EUR 18591, 2000), se establece que un alimento funcional "*puede ser un alimento natural o uno al que se le ha añadido o eliminado componentes, por vía tecnológica o biotecnológica, de forma que se ha demostrado satisfactoriamente que tiene un efecto beneficioso para la salud además de los efectos nutricionales habituales"*.

Aunque la importancia actual del mercado de los alimentos funcionales es variable y difícil de determinar, está claro que tiene un elevado potencial de crecimiento, lo que ha despertado un gran interés en la industria agroalimentaria (Sloan, 2000, 2004). En Estados Unidos, la cuota de

mercado de los alimentos funcionales, en la que se incluyen aquellos que informan sobre los beneficios que pueden aportar a la salud y aquellos que no aportan ninguna información sobre este punto, ha sido, en el año 2000, del 2% del mercado total de alimentos y bebidas. En Europa, a pesar del crecimiento experimentado en la última década, la cuota de mercado de los alimentos funcionales en el mismo año no ha llegado al 1%. Aunque no hay datos concretos, en general, el interés de los europeos de los países centrales y del norte (Alemania, Francia, Reino Unido y Holanda) por este tipo de alimentos es superior al que muestran los habitantes de los países mediterráneos. No obstante, las estimaciones indican que el consumo de alimentos funcionales en Europa tiende a incrementarse considerablemente y puede llegar a alcanzar una cuota del mercado de alimentos y bebidas cercana al 5%, en los próximos 10 años (Menrad, 2003). Recientemente, un informe realizado por Mintel (www.foodanddrinkeurope.com 17/5/2004) confirmó las buenas expectativas del mercado de alimentos funcionales en el Reino Unido, que, después de multiplicar por seis su valor desde 1998 a 2003, es de esperar que lo duplique en los próximos cinco años. Además de esta información, el citado informe ponía de manifiesto que las mejores expectativas de este sector del mercado se centraban en el mercado de las bebidas y de los productos semisólidos, mas fáciles y cómodos de consumir que los alimentos sólidos.

Aparte de estas buenas expectativas, hay que tener en cuenta que el desarrollo de nuevos alimentos funcionales es más arriesgado y costoso que el de los convencionales y requiere no sólo potenciar la investigación sobre nuevos componentes beneficiosos para la salud (Dillard y German, 2000; Madley, 2001) sino también, seleccionar o desarrollar el alimento adecuado para asegurar la estabilidad y biodisponibilidad de cada principio activo (Clydesdale, 2004), poner a punto o mejorar los procesos tecnológicos para elaborarlos con garantías, mejorar los sistemas para asegurar y controlar su

calidad y desarrollar los canales que permitan informar de sus ventajas a los potenciales consumidores (Kwak y Jukes, 2001). Aún resolviendo estos puntos, el éxito de un alimento funcional en el mercado va a depender de que responda a las necesidades del consumidor y del grado de satisfacción que sea capaz de proporcionarle (Heldman, 2004). Por ello, la opinión del consumidor debe ser tenida en cuenta no sólo para evaluar la aceptabilidad del producto final sino desde el inicio del proceso de su desarrollo (van Kleef et al, 2002, Sijtsema et al, 2002). Desde el punto de vista de la investigación, el desarrollo y puesta a punto de nuevos alimentos funcionales requiere la colaboración de distintos especialistas (tecnólogos de alimentos, nutricionistas, fisiólogos, bioquímicos, etc) para obtener nuevos productos con las características de calidad habituales en los alimentos tradicionales (Fogliano y Vitaglione, 2005)

Los alimentos funcionales no están homogéneamente distribuidos entre los distintos sectores del mercado alimentario. El sector de los productos lácteos es uno de los que más ha cambiado por la introducción de nuevos productos con características saludables. A los productos ya tradicionales como los desnatados o con características probióticas, como el yogur, se ha añadido en los últimos años una amplia gama de leches fermentadas de carácter pre- o probiotico, yogures con fitoesteroles o con fibras y de leche enriquecida con fibra o con vitaminas y minerales, con ácidos grasos omega-3, etc. Según Playne et al. (2003), en 2003, el mercado de los productos funcionales lácteos supuso un valor superior a 5.000 millones de dólares. En Europa, el mercado de los alimentos funcionales está dominado principalmente por los probióticos y entre ellos, los lácteos son los mas consumidos. Por ejemplo, en Alemania, en el período 1999-2000, aparecieron en el mercado 305 nuevos productos funcionales de los que un importante porcentaje (20%) fueron productos lácteos (Menrad, 2003). En España, no se ha encontrado información sobre el consumo actual de alimentos funcionales lácteos pero

PRESENTACIÓN DE LOS TRABAJOS Y JUSTIFICACIÓN DE LA UNIDAD TEMÁTICA

Las publicaciones incluidas en la Tesis "**Influencia de la composición en las propiedades físicas y sensoriales de postres lácteos semisólidos"** se dividen en siete capítulos:

***Capítulo 1*. Tárrega, A.**, Durán, L., Costell, E. (2004). Flow behaviour of semisolid dairy desserts. Effect of temperature. *International Dairy Journal*, 14 (4) 345-353

***Capítulo 2.* Tárrega, A.**, Durán, L., Costell, E. (2005). Rheological characterization of semisolid dairy desserts. Effect of temperature. *Food Hydrocolloids* 19 (1) 133-139

***Capítulo 3.* Tárrega, A.** & Costell, E. Colour and consistency of semi-solid dairy desserts. Instrumental and sensory measurements. Enviado a*: Journal of Food Engineering*

***Capítulo 4.* Tárrega, A.**, Costell E. & Rao, M.A. Vane yield stress of native and cross-linked starch dispersions in skim milk: effect of starch concentration and λ-carrageenan addition. *Food Science Technology International* (aceptado)

***Capítulo 5.* Tárrega, A. ,** Vélez-Ruiz, J.F. & Costell, E. (2005). Influence of milk on the rheological behaviour of crosslinked waxy maize and tapioca starch dispersions. *Food Research International* 38 (7) 759-768

***Capítulo 6.* Tárrega, A.** & Costell, E. Effect of composition on viscoleastic behaviour and sensory properties of semisolid dairy desserts. Enviado a: *Food Hydrocolloids*

Capítulo 7. **Tárrega, A.** & Costell, E. Effect of inulin addition on rheological and sensory properties of fat free starch based dairy desserts. Enviado a: *International Dairy Journal*

En los dos primeros capítulos se incluye la información referente a la caracterización del comportamiento reólogico, a las dos temperaturas habituales de consumo (5 y 25ºC), de una serie de muestras comerciales de natillas de vainilla, seleccionadas entre la existentes en el mercado, de forma que representaran la oferta comercial de este producto. Una vez puestas de manifiesto las claras diferencias en el comportamiento de flujo y en la viscoelasticidad de las muestras comerciales y la distinta influencia que las temperaturas ensayadas tenían en sus características reológicas, en el tercer capítulo se abordó el estudio de la relación entre las diferencias de color y de consistencia medidas instrumentalmente y las percibidas sensorialmente.

Los capítulos 4 y 5, tratan de dilucidar los efectos de distintos tipos de almidón y de la leche en distintos aspectos del comportamiento reológico de las dispersiones lácteas de almidón. En el primero de ellos se analiza la influencia de la concentración y del tipo de almidón (nativo y modificado) y de la concentración de λ-carragenato en la resistencia inicial a fluir. En el segundo, se analizan las diferencias entre las dispersiones acuosas y lácteas de tres almidones modificados, dos de maíz y uno de tapioca.

Con la información obtenida en los capítulos anteriores, se seleccionó uno de los almidones modificados, para elaborar sistemas modelo de postres lácteos de vainilla y analizar la influencia del contenido en grasa, de la concentración de λ-carragenato y de la adición de inulina en el comportamiento reológico y en la textura y en el sabor percibidos sensorialmente. En el capitulo sexto, se analizó la influencia de la grasa y de

la concentración de λ-carragenato y en el séptimo, la influencia de la grasa y de la adición de inulina.

Todos los trabajos de esta tesis están orientados hacia el mismo fin, establecer la relación entre la composición de los postres lácteos semisólidos y sus características físicas y sensoriales para poder definir, hasta que punto, la modificación del contenido en grasa o la adición de la inulina pueden modificar dichas características y poder establecer los criterios que permitan optimizar la calidad de estos productos.

OBJETIVOS

El objetivo general de esta investigación fue:

Obtener información sobre la influencia de la composición en las características físicas y sensoriales de postres lácteos semisólidos, aplicable al diseño y optimización de la formulación de nuevos alimentos funcionales.

Para conseguirlo, se establecieron los siguientes objetivos específicos:

- Caracterizar el comportamiento reológico de las natillas comerciales españolas y estudiar la relación entre las medidas instrumentales y sensoriales de su color y de su textura.
- Analizar la influencia del tipo y de la concentración de almidón en el comportamiento de flujo y en la viscoelasticidad de las dispersiones lácteas de diferentes almidones.
- Analizar la influencia del contenido en grasa y de la adición de inulina en las propiedades reológicas y sensoriales de sistemas modelo de postres lácteos gelificados.

según el MAPA (2004), de 2002 a 2003 el consumo de leche disminuyó en un 1.87%, mientras que el de derivados lácteos y otras leches se incrementó en un 3.68%. De hecho, en 2003, el gasto *per cápita* en derivados lácteos supuso el 7.2% del consumo alimentario en los hogares españoles mientras que el de leche, solo alcanzó un porcentaje del 4.4%. Es lógico deducir que esta evolución en el consumo de distintos productos lácteos está relacionada con el incremento de productos funcionales lácteos en el mercado.

Los postres lácteos semisólidos de diferentes sabores (vainilla, chocolate, fresa, etc) son productos muy populares en Europa. Entre ellos, los de vainilla ("Natillas" en España, "Vanilla vla" en Holanda o "Crème dessert"en Francia), son los más consumidos. Sus características nutricionales y sensoriales los hacen especialmente adecuados para diferentes grupos de consumidores como los niños y las personas mayores. Básicamente, están compuestos por leche, espesantes (almidón e hidrocoloides), sacarosa, aroma de vainilla y colorantes. Las características de estos ingredientes- el contenido en grasa de la leche, el tipo y concentración de almidón, el tipo y concentración de hidrocoloide, la concentración de sacarosa, el aroma y el colorante-y las interacciones entre ellos, pueden dar lugar a importantes diferencias en las propiedades físicas y sensoriales de estos productos y estas diferencias pueden influir en la aceptación de los mismos por los consumidores. Existe muy poca información sobre las características físicas y sensoriales de estos productos. Batista et al (2002) caracterizaron el flujo y la viscoelasticidad de dos muestras comerciales portuguesas de postres lácteos gelificados para analizar, hasta que punto, la sustitución de la leche por proteínas vegetales modificaba su comportamiento reológico y De Wijk, et al (2003) investigaron los perfiles sensoriales de 12 muestras comerciales de natillas holandesas y encontraron claras diferencias perceptibles entre ellas principalmente en dos atributos de textura: la consistencia y la cremosidad.

Otros autores, utilizando sistemas modelo de postres lácteos, han estudiado el efecto de algunos de los ingredientes en su textura, comportamiento reológico y sabor para intentar dilucidar la contribución de cada componente a las características del producto final. Parker y Tilly (1994) analizaron la influencia de la adición de ί-carragenato en la dependencia del tiempo de su flujo y de Vries (2002), la de diferentes tipos de carragenato en la firmeza de geles lácteos de almidón. En el mismo tipo de sistemas, Wischmann et al (2002) estudiaron el efecto de la concentración de almidón en su comportamiento de flujo y en su viscoelasticidad y concluyeron que la dependencia del tiempo de su flujo y su comportamiento viscoelástico se debían a su estructura gelificada y Depeyre, et al. (2003) analizaron el efecto de las interacciones entre el κ-carragenato, el almidón de maíz y las proteínas lácteas en la viscoelasticidad y en la resistencia a la compresión de diferentes sistemas modelo de postres lácteos. Lethuaut, et al (2003) estudiaron el efecto de la concentración de azúcar y de la adición de distintos tipos de carragenato en la textura de postres lácteos de vainilla y el impacto que la modificación de su textura tenía en el sabor. Concluyeron que la firmeza de los sistemas modelo que contenían κ- y λ-carragenato, la elasticidad de los elaborados con ί-carragenato y la untuosidad de los de λ-carragenato se incrementaba al hacerlo la concentración de sacarosa y que para una misma concentración de ésta, el dulzor percibido en las diferentes muestras dependía del tipo de carragenato utilizado. Esta información confirma que las interacciones entre los distintos ingredientes pueden dar lugar a productos con características físicas y sensoriales muy distintas y que la investigación de los efectos de estas interacciones puede aportar una información muy interesante para la formulación de nuevos productos.

Aparte de la indudable importancia económica de los productos lácteos fermentados, sobre todo del yogur y de algunos tipos de bebidas lácteas, una de las posibilidades de desarrollo de nuevos alimentos funcionales lácteos es

la eliminación o sustitución de determinados ingredientes (grasa, azúcar) o la adición de determinados compuestos de características saludables contrastadas (fibra soluble, omega-3, vitaminas, fitoesteroles, etc) en las formulaciones de productos lácteos convencionales. Es obvio que este tipo de acciones, además de incrementar los efectos beneficiosos del alimento en la salud, también pueden modificar su composición y su estructura. Estas modificaciones pueden dar lugar a variaciones en sus atributos sensoriales e incidir directamente en la aceptabilidad del producto.

Tal como se ha comentado, los postres lácteos gelificados, tipo natillas, tienen unas características sensoriales, que unidas a la facilidad con que se ingieren, los hacen aceptables para un amplio espectro de consumidores. Uno de los problemas que plantean para ciertos sectores de la población es que son muy calóricos y tienen un alto contenido en grasa. La eliminación o reducción de este contenido podría convertirlos en una alternativa válida a otros productos lácteos bajos en grasa, ampliando la gama de productos disponibles para consumidores con determinados requerimientos dietéticos. Por otro lado, la inclusión en su formulación de algún ingrediente con características saludables específicas, como la inulina, podría convertirlos en un alimento funcional de características diferentes a los habituales en el mercado.

La inulina es un fructooligosacárido no digestible que aporta al hombre no solo los beneficios inherentes a su condición de fibra dietética (reducción de los niveles de lípidos y de colesterol en la sangre, regulación del tránsito intestinal, incremento de la adsorción de calcio, etc) (Flamm et al., 2001) sino también los derivados de su carácter prebiótico, relacionados con la estimulación del crecimiento de las bifidobacterias (Roberfroid et al.,1998) y con la regulación de la flora intestinal del colon (Kaur y Gupta, 2002). Además de su efecto beneficioso para la salud, la inulina se está utilizando en la formulación de nuevos alimentos por sus propiedades tecnológicas,

como sustituto de grasa, como edulcorante o por su capacidad para modificar la textura (Tungland y Meyer, 2002). Sus propiedades como sustituto de grasa se atribuyen a su capacidad para enlazar moléculas de agua y para formar una estructura gelificada (Frank, 2002). Aunque se está empezando a utilizar como sustituto de la grasa en la formulación de algunos productos lácteos, como en helados (El-Nagar et al.,2002; Schaller-Polovny y Smith, 1999 y 2001) yogures (El-Nagar et al.,2002) o queso fresco (Koka y Metin, 2004) existe muy poca información sobre sus características físicas y tecnológicas y sobre el efecto de sus posibles interacciones con los otros componentes o ingredientes del alimento.

Para diseñar y desarrollar nuevos productos funcionales que, además de aportar beneficios específicos para la salud, sean aceptables para el consumidor, es necesario conocer hasta qué punto la modificación de su composición influye en su aceptabilidad. En este contexto, la investigación de la influencia de la composición en las propiedades físicas y sensoriales de un alimento es el primer paso para desarrollar nuevos productos saludables y que satisfagan los requerimientos del consumidor.

Bibliografía

Andlauer, W. & Fürst, P (2002). Nutraceuticals:a piece of history, present status and outlook. *Food Research International*, 35, 171-176.

Batista, P., Nunes, M.C. & Sousa, I. (2002). Physical characterisation of commercial dairy desserts. In F.J. Martínez Boza, A. Guerrero, P. Partal, J.M. Franco & J. Muñoz., *Progress in Rheology Theory and Applications.* Publicaciones Digitales S.A. Sevilla, Spain, 449-452.

Bello, J. (2001) Alimentos para la salud. Arbor, 661, 1-29.

Clydesdale, F. (2004). Functional Food: Opportunities & Challenges. *Food Technology*, 58, 12: 35-40.

De Vries, J. (2002). Interaction of carrageenan with other ingredients in dairy dessert gels. En P.A. Williams and G.O. Philips, *Gums and stabilisers for the food industry 11*. Royal Society of Chemistry, Cambridge, UK, 201-210.

De Wijk, R. A., Rasing, F. & Wilkinson, C. L. (2003). Texture of semi-solids: Sensory flavor-texture interactions for custard desserts. *Journal of Texture Studies*, 34, 131-146.

Depypere, F., Verbeken, D., Thas, O. & Dewettinck, K. (2003). Mixture design approach on the dynamic rheological and uniaxial compression behaviour of milk desserts. *Food Hydrocolloids*, 17, 311-320.

Dillard, C.J. & German, J.B. (2000). Phytochemicals: Nutraceuticals and human health. Review. *Journal Science of Food and Agriculture*, 80, 1744-1756

El-Nagar, G., Clowes, G., Tudorica, C.M., Kuri, V. & Brennan, C.S. (2002). Rheological quality and stability of yog-ice cream with added inulin. *International Journal of Dairy Technology*, 55, 89–93.

EUR 1859 (2000). Scientific concepts of functional foods in Europe. Project Report. Vol.3. Dg research-RTD actions: life sciences and technologies. Bruselas. Bélgica.

Flamm, W. Glinsmann, D., Kritchevsky, L., Prosky, M. Roberfroid, M.B. (2001). Inulin and oligofructose as dietary fiber: a review of the evidence. *Critical Reviews in Food Science and Nutrition,* 41, 353–362.

Fogliano, V. & Vitaglione, P. (2005). Review: Functional Foods: Planning and development. *Molecular Nutrition & Food Research*, 49, 256-262.

Franck, A. (2002). Technological functionality of inulin and oligofructose. *British Journal of Nutrition*, 2, 287-291.

Hasler, C.M. (1998) Functional foods: Their role in disease prevention and health promotion. *Food Technology*, 52, 63-70.

Hasler, C.M. (2000) The changing face of functional foods. *Journal of American College of Nutrition*, 19, 499-506.

Heldman, D. R. (2004). Identifying Food Science & Technology Research Needs. Food Technology, 58,12 32-34.

Holzapfel, W.H. & Schillinger, U. (2002) Introduction to pre and probiotics. Food Research International, 32, 109-116.

IFT (1992). Medical foods. A scientific status summary by the Institute of Food Technologists' Expert Panel on Food Safety and Nutrition. *Food Technology* 46, 87-96.

Kaur, N. & Gupta, A. K. (2002). Applications of inulin and oligofructose in health and nutrition. *Journal of Biosciences*, 27, 703-714.

Koca, N. & Metin, M. (2004) .Textural, melting and sensory properties of low-fat fresh kashar cheeses produced by using fat replacers. *International Dairy Journal*, 14, 365-373.

Kwak NS, Jukes D. (2001) Issues in the substantation process of health claims. *Critical Reviews in Food Science and Nutrition*, 41, 465-479.

Lethuaut, L., Brossard, C., Rousseau, F., Bousseau, B. & Genot. C. (2003). Sweetness-texture interactions in model dairy desserts: effect of sucrose concentration and the carrageenan type. *International Dairy Journal*, 13, 631-641.

Madley, R.H. (2001). Probiotics, Prebiotics & Synbiotics: Harnessing enormous Potential. Nutraceuticals World, September, 50-76.

MAPA (2004). Hechos y cifras de la agricultura, la pesca y la alimentación en España. www.mapya.es/alimentación.

Parker, A. & Tilly, G. (1994). Thixotropic carrageenan gels and dairy desserts. In G.O. Philips., P.A. Williams and D.J. Wedlock, *Gums and stabilisers for the food industry 7*. IRL Press, Oxford, UK, 393-401.

Playne, MJ., Bennett, L.E. & Smithers, G.W. (2003). Functional dairy foods and ingredients. *Australian Journal of Dairy Technology*, 48, 242-264.

Roberfroid, M.B., Van Loo, J.A E. & Gibson, G.R. (1998). The bifidogenic nature of chicory inulin and its hydrolysis products. *Journal of Nutrition*, 128, 11-19.

Schaller-Povolny, L.A. & Smith D.E. (1999). Sensory attributes and storage life of reduced fat ice cream as related to inulin content. *Journal of Food Science*,64, 555–559.

Schaller-Povolny, L.A. & Smith, D.E. (2001) .Viscosity and freezing point of a reduced fat ice cream mix as related to inulin content. *Milchwissenschaft-Milk Science International*, 56, 25-29.

Sijtsema, S., Linnemann, A., van Gaasbeek, T., Dagevos, H. & Jongen. W. (2002) Variables influencing food perception reviewed for consumer-oriented product development. *Critical reviews Food Science and Nutrition*, 42, 565-581.

Sloan, E. (2000) The Top Ten Functional Food Trends. *Food Technology*, 54, 4, 33-62.

OBJETIVOS

El objetivo general de esta investigación fue:

Obtener información sobre la influencia de la composición en las características físicas y sensoriales de postres lácteos semisólidos, aplicable al diseño y optimización de la formulación de nuevos alimentos funcionales.

Para conseguirlo, se establecieron los siguientes objetivos específicos:

- Caracterizar el comportamiento reológico de las natillas comerciales españolas y estudiar la relación entre las medidas instrumentales y sensoriales de su color y de su textura.
- Analizar la influencia del tipo y de la concentración de almidón en el comportamiento de flujo y en la viscoelasticidad de las dispersiones lácteas de diferentes almidones.
- Analizar la influencia del contenido en grasa y de la adición de inulina en las propiedades reológicas y sensoriales de sistemas modelo de postres lácteos gelificados.

PRESENTACIÓN DE LOS TRABAJOS Y JUSTIFICACIÓN DE LA UNIDAD TEMÁTICA

Las publicaciones incluidas en la Tesis "**Influencia de la composición en las propiedades físicas y sensoriales de postres lácteos semisólidos"** se dividen en siete capítulos:

***Capítulo 1*. Tárrega, A.**, Durán, L., Costell, E. (2004). Flow behaviour of semisolid dairy desserts. Effect of temperature. *International Dairy Journal*, 14 (4) 345-353

***Capítulo 2.* Tárrega, A.**, Durán, L., Costell, E. (2005). Rheological characterization of semisolid dairy desserts. Effect of temperature. *Food Hydrocolloids* 19 (1) 133-139

***Capítulo 3.* Tárrega, A.** & Costell, E. Colour and consistency of semi-solid dairy desserts. Instrumental and sensory measurements. Enviado a*: Journal of Food Engineering*

***Capítulo 4.* Tárrega, A.**, Costell E. & Rao, M.A. Vane yield stress of native and cross-linked starch dispersions in skim milk: effect of starch concentration and λ-carrageenan addition. *Food Science Technology International* (aceptado)

***Capítulo 5.* Tárrega, A. ,** Vélez-Ruiz, J.F. & Costell, E. (2005). Influence of milk on the rheological behaviour of crosslinked waxy maize and tapioca starch dispersions. *Food Research International* 38 (7) 759-768

***Capítulo 6.* Tárrega, A.** & Costell, E. Effect of composition on viscoleastic behaviour and sensory properties of semisolid dairy desserts. Enviado a: *Food Hydrocolloids*

Capítulo 7. **Tárrega, A.** & Costell, E. Effect of inulin addition on rheological and sensory properties of fat free starch based dairy desserts. Enviado a: *International Dairy Journal*

En los dos primeros capítulos se incluye la información referente a la caracterización del comportamiento reólogico, a las dos temperaturas habituales de consumo (5 y 25ºC), de una serie de muestras comerciales de natillas de vainilla, seleccionadas entre la existentes en el mercado, de forma que representaran la oferta comercial de este producto. Una vez puestas de manifiesto las claras diferencias en el comportamiento de flujo y en la viscoelasticidad de las muestras comerciales y la distinta influencia que las temperaturas ensayadas tenían en sus características reológicas, en el tercer capítulo se abordó el estudio de la relación entre las diferencias de color y de consistencia medidas instrumentalmente y las percibidas sensorialmente.

Los capítulos 4 y 5, tratan de dilucidar los efectos de distintos tipos de almidón y de la leche en distintos aspectos del comportamiento reológico de las dispersiones lácteas de almidón. En el primero de ellos se analiza la influencia de la concentración y del tipo de almidón (nativo y modificado) y de la concentración de λ-carragenato en la resistencia inicial a fluir. En el segundo, se analizan las diferencias entre las dispersiones acuosas y lácteas de tres almidones modificados, dos de maíz y uno de tapioca.

Con la información obtenida en los capítulos anteriores, se seleccionó uno de los almidones modificados, para elaborar sistemas modelo de postres lácteos de vainilla y analizar la influencia del contenido en grasa, de la concentración de λ-carragenato y de la adición de inulina en el comportamiento reológico y en la textura y en el sabor percibidos sensorialmente. En el capitulo sexto, se analizó la influencia de la grasa y de

la concentración de λ-carragenato y en el séptimo, la influencia de la grasa y de la adición de inulina.

Todos los trabajos de esta tesis están orientados hacia el mismo fin, establecer la relación entre la composición de los postres lácteos semisólidos y sus características físicas y sensoriales para poder definir, hasta que punto, la modificación del contenido en grasa o la adición de la inulina pueden modificar dichas características y poder establecer los criterios que permitan optimizar la calidad de estos productos.

FLOW BEHAVIOUR OF SEMI-SOLID DAIRY DESSERTS. EFFECT OF TEMPERATURE*

A. Tárrega, L. Durán, & E. Costell **

Instituto de Agroquímica y Tecnología de Alimentos. CSIC.
P.O. Box 73. 46100 Burjassot (Valencia). Spain.

Abstract

The flow behaviour of seven commercial samples of *natillas*, a popular semisolid dairy dessert in Spain, was analysed at the two common consumption temperatures, 5 and 25ºC, with special attention to their time dependent properties. All samples showed time dependence at both temperatures tested. For the same temperature, differences in the form and in the magnitude of the hysteresis loop were observed among samples, these differences being more noticeable at 5ºC. An analysis of variance of the thixotropic area values, considering sample and temperature as factors, showed a significant interaction between these factors (F_{int} = 53.21, p= 0.000), which indicates that the effect of temperature on this area was different depending on samples. Similar results were obtained by analysing Weltmann parameters A and B, from shear stress decay experiments. Shear stress decay data fitted well to a second order structural kinetics model $[(\eta_0-\eta_e)/(\eta-\eta_e)] = kt +1$, and the sample-temperature interaction was also significant on parameter k from this model (F_{int} = 5.46**,** p=0.004). Flow of samples, after eliminating thixotropy, fitted well to the Herschel-Bulkley model ($\sigma=\sigma_0+K\dot{\gamma}^n$). Here again, sample-temperature interactions were significant for σ_0 (F_{int} = 5.40, p=0.005) and for η_1 (F_{int} = 6.63, p=0.002). Although the extent of the differences varied among samples, in general, time dependence, plasticity and consistency were lower and pseudoplasticity was slightly higher at the higher temperature.

Keywords: Flow behaviour, Flow time dependence, Dairy desserts, Shear thinning, Structural kinetics model

---

* Part of this paper was presented as a poster at "The Third Nizo Dairy Conference", Papendal, The Netherlands, 11-13 June

**Corresponding author. Tel.:+34-96-3900022; Fax: +34-96-3636301.
E-mail adress: ecostell@iata.csic.es (E.Costell).

1. Introduction

The “natillas”, a semisolid dairy dessert of wide consumption in Spain, are composed of milk, starch, hydrocolloids, sugars, colorants and aromas. The particular characteristics of some ingredients, like fat content of milk, type of starch, and/or type and concentration of hydrocolloids, and their crossed interactions, will be reflected in notable differences in the rheological and sensory properties, as reported for similar products (Nadison & Doreau, 1992, Descamps, Langevin & Combs, 1986). Little information is available on the differences to be found in commercial samples of this type of dairy desserts. Recently, Wijk, van Gemert, Terpstra and Wilkinson (2003) analysed the differences in sensory texture in 12 commercial samples of vanilla custard dessert (called “vla” in Dutch), and related them to their composition. Wischmann, Norsker and Adler-Nissen (2002) studied the effects of starch concentration on both flow behaviour and viscoelasticity of dairy cream model systems and observed that they all showed time dependent and pseudoplastic flow and that their viscoelastic nature was due to a gelled structured. The same type of behaviour was observed before by Longrée, Behaver, Buck and Nowrey (1966) in another type of dairy cream model system containing egg, besides milk and starch.

In general, the flow properties of this type of products, e.g. time dependence and pseudoplasticity, follow the same pattern as those of starch pastes, whose rheological behaviour responds to the resistance to shear of a biphasic structure defined by the characteristics of the dispersed phase (starch granules) and by the viscosity of the dispersing phase (Nguyen, Jensen & Kristensen, 1998; Thebaudin, Lefebvre, & Doublier, 1998). Quantitative changes in the rheological response of these systems may be originated by substituting milk for water in starch pastes (Matser & Steeneken, 1997), by adding different types of hydrocolloids (Umadevi & Raghavendra,1987; Alloncle & Doublier, 1991; Liu & Eskin, 1998) or by changes in the

experimental elaboration process (Nayouf, Loisel & Doublier, 2003). As reported by Tecante and Doublier (1999), the rheological behaviour of mixtures of starch and hydrocolloids is determined by their composition and by the experimental conditions of the elaboration process. Specially relevant is the effect of the cooking operation on the physical characteristics of the starch granules.

Rheological characterisation of flow-time dependent fluids is not easy (Tiu & Boger, 1974). That their apparent viscosity does not depend only on shear rate but also on the time shear is applied. Experimentally the flow time dependence is clearly shown by running an hysteresis cycle. The hysteresis area will give an estimate of the magnitude of the product thixotropy (Longrée et al., 1966; Barbosa-Cánovas & Peleg, 1983; Carbonell, Costell & Durán, 1991a; Thebaudin et al., 1998). A more common way to quantify this characteristic is to register the shear stress decay with time of application of a constant shear rate and fit the experimental data to an empirical mathematical model like the well known Weltmann's model (1943) or to a theoretical one like that of Hahn, Ree and Eyring (1959). Structural kinetics models (Tiu & Boger, 1974; Nguyen & Boger, 1985), based on the previous structural theory proposed by Cheng and Evans (1965) have been used. According to this theory, the change with time of the rheological properties of a material is associated with the destruction by shearing of its internal structure in such a manner that its rheological behaviour may be modelled by two equations: a state equation providing the instantaneous shear stress value as a function of shear rate and of the corresponding structural parameter value, and a kinetic equation describing the evolution of the structural parameter with time.

The objectives of this paper are to characterise the flow behaviour of commercial samples of Spanish "natillas" with special attention to their time

dependent properties, and to study the effect of the consumption temperature on their rheology.

2. Experimental

2.1. Materials

Samples of vanilla dairy desserts (*natillas*) of seven different brands, covering the commercial range, were purchased from the local market. Their main characteristics are given in Table 1. The samples were stored at 4±1ºC prior to testing and all measurements were performed within the shelf-life period of each sample.

Table 1. Main composition and price level of commercial vanilla cream dairy desserts samples.

Sample	Dairy ingredients [a]	Thickeners [a]	pH [b]	Soluble solids [b] (º Brix)	Price[c]
1	Semi-skimmed milk	Modified starch Carrageenan Xanthan gum	6.81	24.5	1.4
2	Milk Semi-skimmed milk	Modified starch Carrageenan Guar gum	6.76	23.7	1
3	Milk Cream Semi-skim milk powder	Acetylated distarch adipate Gelatine	6.61	28.3	2.3
4	Milk Cream Dairy solids	Modified starch Carrageenan Fatty acid esters	6.60	26.3	2.5
5	Milk Cream	Modified starch Carrageenan Guar gum	6.76	23.5	2.5
6	Milk Cream	Modified starch Carrageenan Guar gum	6.72	24.5	1.7
7	Milk Cream Dairy solids	Modified starch Carrageenan Fatty acid esters	6.75	24.5	1.9

a. Declared in label.
b. Average value of two measurements
c. Lower price considered as reference unit

2.2. Methods

2.2.1. Soluble solids and pH

Soluble solids were determined at room temperature (20-22ºC) with an ATAGO RX-100 digital refractometer and the results given as degrees Brix at 20ºC. A CRISON digital potentiometer was used to measure pH at room temperature. Both measurements were done twice in each sample.

2.2.2. Rheological measurements

The measurements were carried out in a Haake VT 550 viscometer, using concentric cylinders sensors (MV1 and MV3, with 1.05 and 1.38 radii ratios, respectively), monitored by a Rheowin Pro software (version 2.93, Haake). The samples were analysed at two temperatures, 5±1 and 25±1ºC, selected as representative of the usual consumption temperatures. Two replicates were run at each test temperature and a fresh sample was loaded for each run.

2.2.2.1. Time dependence

The samples were allowed to rest 15 min after loading, before measurement. Two methods were applied: Hysteresis loop and Shear stress decay.

The hysteresis loop was obtained by registering shear stress at shear rates from 1 to 200 s^{-1} in 60 s and down in 60 s. Areas under the upstream data points (A_{up}) and under the downstream data points (A_{down}) as well as the hysteresis area (A_{up} - A_{down}) were obtained using Rheowin Pro software (version 2.93, Haake).The percentage of relative hysteresis area (Longrée et al., 1966; Dolz, González, Delegido, Hernández, & Pellicer, 2000) was calculated by equation [1]:

$$A_r = (A_{up} - A_{down})/ A_{up} \times 100 \qquad [1]$$

The shear stress decay was determined by applying a shear rate of 100 s^{-1} during 900 s. Experimental data were fitted to the Weltmann (1943) model and to the structural kinetic model of Nguyen et al. (1998).

Fitting to the Weltmann model [2] was performed using the Rheowin Pro software (version 2.93, Haake):

$$\sigma = A - B \ln t \qquad [2]$$

where A is the initial shear stress and B, the time coefficient of thixotropic breakdown.

Nguyen et al. (1998) developed a structural kinetic model to characterise time dependence in starch pastes, due to the irreversible breakdown of network structures produced by shearing. According to these authors, the structured state of the material at any time *t* and under an applied shear rate γ can be represented by a dimensionless parameter $\Psi=\Psi(t,\dot{\gamma})$, defined as

$$\Psi(t,\dot{\gamma}) = (\eta-\eta_e)/(\eta_0-\eta_e) \qquad [3]$$

where η_0 is the initial apparent viscosity at t=0 and η_e is the equilibrium apparent viscosity at $t\rightarrow\infty$.

Considering the network structural breakdown as a chemical reaction, the rate of breakdown will be given by

$$-d\Psi/dt = k(\Psi-\Psi_e)^m \qquad [4]$$

where m is the kinetic order.

Integrating equation [4]:

$$(\Psi-\Psi_e)^{1-m} = (m-1)\, kt + (\Psi_0-\Psi_e)^{1-m} \qquad [5]$$

Substituting equation [3] into equation [5]:

$$[(\eta-\eta_e)/(\eta_0-\eta_e)]^{1-m} = (m-1)kt + 1 \qquad [6]$$

Variation of apparent viscosity values at 100 s^{-1} with time, determined in our study, fitted well to equation [6], considering a second order kinetics with m=2.

2.2.2.2. Flow behaviour

Before analysing flow behaviour, the structure responsible for thixotropy was previously destroyed by shearing (Halmos & Tiu, 1981; Carbonell et al., 1991a; Nguyen et al., 1998; Abu-Jydail, 2002). After testing several shearing conditions, five minutes at 100, 200, and 300 s^{-1} shear rates, and analysing the hysteresis cycles, a previous shearing of five minutes at 300 s^{-1} was selected as the appropriate treatment to get a nule hysteresis area.

After eliminating time dependence, sample flow was measured by registering shear stress values when shearing the samples at increasing shear rates from 1 to 200 s^{-1}. Data obtained were fitted to Herschel-Bulkley model ($\sigma=\sigma_0+K\dot{\gamma}^n$) [7] using the Rheowin Pro software (version 2.93, Haake). The yield stress (σ_0) value, used in Herschel-Bulkley's model, was previously obtained by fitting the experimental data to the Casson model ($\sigma^{0.5}=\sigma_0^{0.5}+K\dot{\gamma}^{0.5}$) [8]. This was taken as the square of the ordinate intercept in the Casson plot (Costell, Carbonell, & Durán, 1993; Skriver, Roemer, & Qvist, 1993). Apparent viscosity values were obtained with the expression $\eta_{ap}= \sigma_0/\dot{\gamma} + K\dot{\gamma}^{n-1}$[9].

2.3. Statistical analysis

The effect of temperature on the different rheological parameters was analysed by two factors (sample and temperature) ANOVA with interactions. The Fisher test (α=0.05) was used to calculate the minimum significant differences. All calculations were carried out with the Statgraphics Plus 4.1 software.

3. Results and discussion

3.1. Influence of temperature on time dependence

3.1.1. Hysteresis area

When a sample is sheared at increasing and then at decreasing shear rates, the observation of the hysteresis area between the curves representing shear stress values indicates that the sample's flow is time dependent. According to Halmos and Tiu (1981), the area encircled between the ascending and the descending curves is an index of the energy per unit time and unit volume needed to eliminate the influence of time in flow behaviour.

All samples showed observable hysteresis at both temperatures tested, 5 and 25ºC (Fig.1). For the same temperature, differences in the form and in the magnitude of the hysteresis loop were observed among samples, these differences being more noticeable at 5ºC. An analysis of variance of the thixotropic area values, considering sample and temperature as factors, showed a significant interaction between these factors, the corresponding F values (F_{int}) being 53.21 (p= 0.000), which indicates that the effect of temperature on this area was different depending on samples. As expected, the loop area was significantly smaller at the higher temperature (α= 0.05)

for all samples. The areas obtained at 25ºC were always less than half the values for 5ºC (Fig. 2).

The value assigned to a certain hysteresis area depends on the loop contour and on the shear resistance of the sample. It can also vary according to the experimental conditions of the test (total shearing time and range of shear rates applied). As reported by Hernández (1996), a high viscosity thixotropic fluid may show a larger hysteresis area than a lower viscosity one even if the

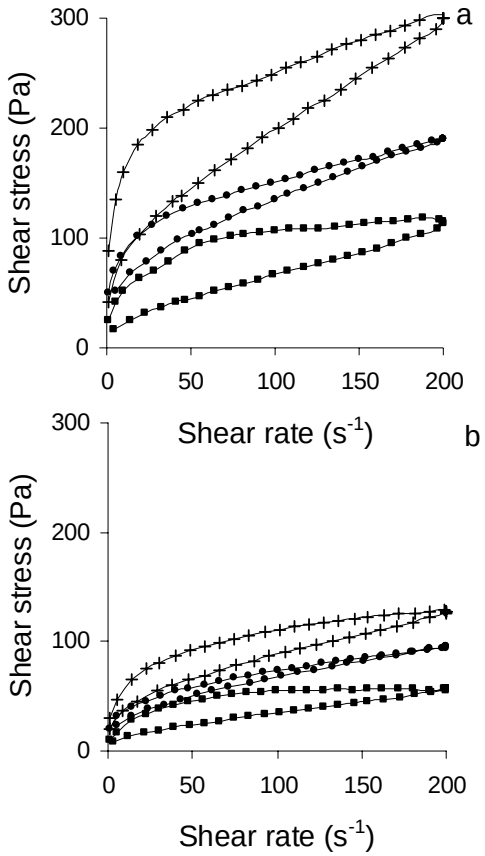

Figure 1. Hysteresis loops obtained for dairy dessert samples: (■) 1, (●● 3, and (+) 7 at 5ºC (a) and at 25ºC (b). Identification of samples in Table 1.

latter undergo a stronger structural destruction. Comparison of straight loop areas between differently viscous systems may not render valid conclusions on the extension of time dependent structural breakdown. In our study, sample 7, showing the largest loop area is also the one showing the highest resistance to flow. An alternative approach may be the use of the relative thixotropic area, defined as the ratio of the "absolute" hysteresis area to the area under the ascending shear curve (Dolz et al., 2000). Considering the relative thixotropic areas, a significant sample-temperature interaction (F_{int} = 5.72, p=0.004) was also found. At the higher temperature (25ºC) the relative areas were smaller (Fig. 3) but the decrease with respect to the values at 5ºC was lower than for the directly registered loop areas (Fig. 2). Also the differences between samples were not the same when the relative areas were compared. Assuming that a hysteresis loop area is an index of the energy needed to destroy the structure responsible for time dependence, the experimental data showed that sample 7 was the one needing the highest energy to breakdown such structure, while if the relative areas are considered the highest energy value was shown by sample 1.

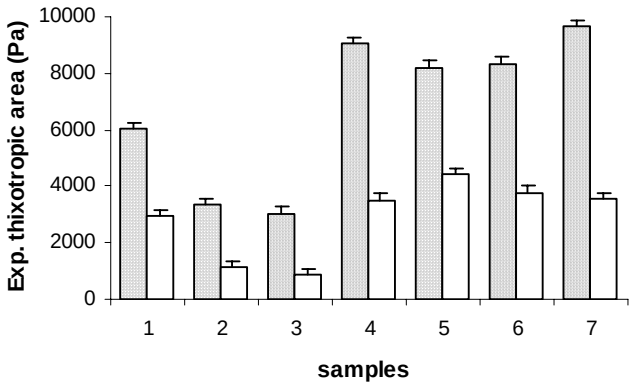

Figure 2. Experimental hysteresis area values of dairy dessert samples at 5ºC (▭) and 25ºC (▭). Identification of samples in Table 1.

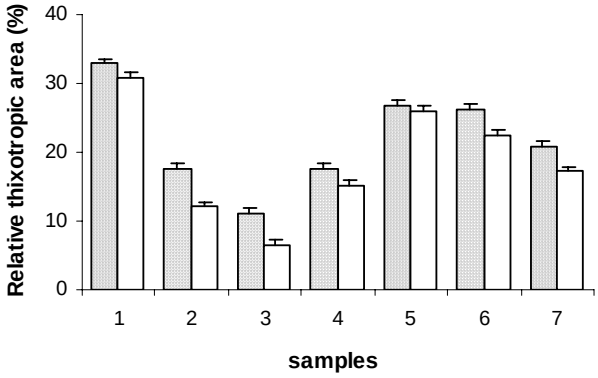

Figure 3. Relative thixotropic area values of dairy dessert samples at 5ºC ( ) and 25ºC ( ). Identification of samples in Table 1.

3.1.2. Shear stress decay test

At a 100 s^{-1} shear rate, the shear stress values decreased rapidly with time within the first 300 s of shearing and approached a constant value, corresponding to an equilibrium state, after approximately 900 s. The rate and extent of shear stress decay varied among samples and between temperatures (Fig. 4). The observed time dependent flow behaviour of samples was modelled using both an empirical equation - the Weltmann model (1943) - and the modified structural kinetics approach proposed by Nguyen et al. (1998).The experimental data fitted well to the Weltmann model, with R^2 values going from 0.920 to 0.998 for all samples and temperatures but in one case. Stress decay in sample 1 fitted rather well to the Weltmann model when measured at 5ºC (R^2= 0.920), but not so when measured at 25ºC (R^2= 0.859). This model has also been considered appropriate to characterise time dependence of the flow of other food products like salad dressings (Paredes, Rao, & Bourne, 1989), fruit jams (Carbonell, Costell, & Durán, 1991b) or yoghurts (O'Donnell & Butler,

2002). As reported above for the hysteresis areas, the stress decay with time of all samples (Fig. 4) showed differences among them at both temperatures, but smaller at the higher temperature.

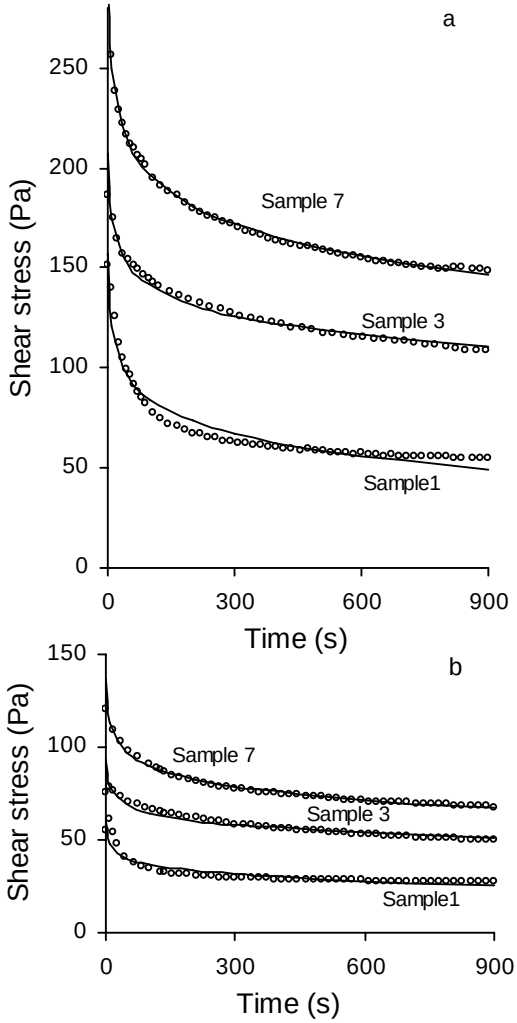

Figure 4. Shear stress decay at a constant shear rate of 100s^{-1} for some dairy dessert samples at 5ºC (a) and at 25ºC (b). Experimental values (○) and fits to Weltmann model (—). Identification of samples in Table 1.

In the Weltmann model, parameter A represents the initial shear stress and parameter B, the time coefficient of thixotropic breakdown, is "the product of rate in breakdown of thixotropic structure and time of agitation at constant rate of shear" (Weltmann, 1943). ANOVA results showed that sample-temperature interaction was significant for both parameters (F_{int} = 66.71, p=0.000 for parameter A and F_{int} = 18.29, p=0.000 for parameter B). At the higher temperature both parameters showed lower values and the difference with the values obtained at 5ºC varied among samples (Fig. 5).

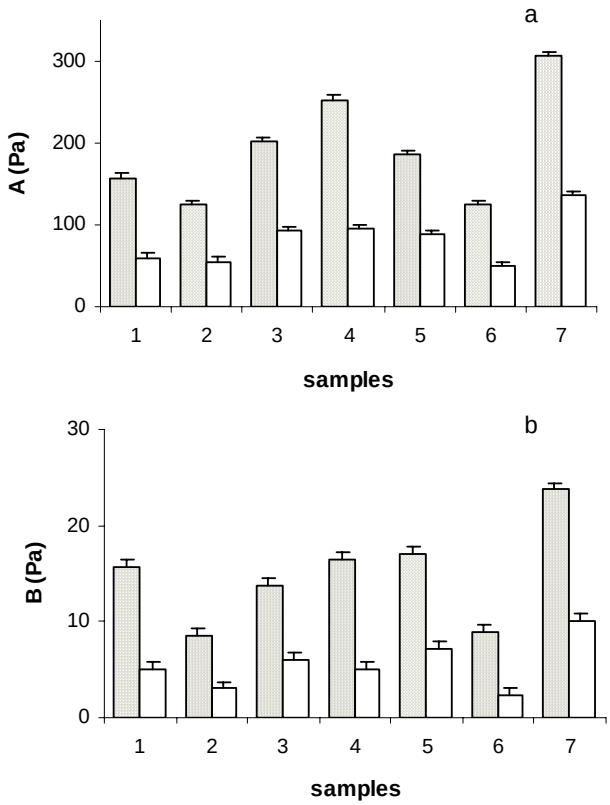

Figure 5. Weltmann A and B parameters values (a and b respectively) of dairy dessert samples at 5ºC ( ) and at 25ºC ( ). Identification of samples in Table 1.

Similar results were reported by Paredes et al. (1989) in commercial samples of salad dressings, for which Weltmann parameters obtained at two temperatures, 2 and 10ºC, showed lower values at the higher temperature but the differences varied among samples.

Sample 7 showed the highest initial stress value at both temperatures, which was less than half at 25º C than at 5ºC (Fig. 5a). Also the B value was higher for sample 7 than for the rest of samples at both temperatures (Fig. 5b), indicating its higher rate of structural breakdown by shearing.

It is interesting to note that the observed variations in the values of Weltmann parameters A and B among samples and the effect of temperature on these parameters (Fig. 5) followed the same pattern as the thixotropic area values (Fig. 2) and that the effect of temperature on these three parameters was stronger than that observed on the relative thixotropic area (Fig. 3).

The structural kinetics model postulates that the change in time-dependent flow properties is associated with shear-induced breakdown of the internal fluid structure and that the rate of this breakdown during shear depends on the kinetics of the *structured state* $\rightarrow$ *non-structured* state process (Abu-Jdayil, 2003). For all samples studied, the transient apparent viscosity data at a shear rate of 100 s^{-1} during the first 400 s of shearing could be satisfactorily modelled with a second order structural kinetic model (m=2) (Fig. 6). The plots of $[(\eta_0-\eta_e)/(\eta-\eta_e) -1]$ versus t for all samples and for both temperatures (5 and 25ºC) were linear ($0.966 < R^2 < 0.995$) which confirmed the applicability to this case of the model:

$$[(\eta_0-\eta_e)/(\eta-\eta_e)] = kt +1 \qquad [10]$$

In this plot (Fig. 6), k values are the slopes of the lines. A good coincidence was found between the model fitted results (solid line) and the experimental transient apparent viscosity data for all samples and for both temperatures (5 and 25ºC) (Fig. 7). In contrast with these results, Nguyen et al (1998)

reported that transient viscosity data, for maize and waxy maize starch pastes, could be fitted to a third order kinetic model.

Table 2. Viscosity ratio (η_0/η_e) and structural breakdown rate constant (k) for the second order kinetic model (average values of two measurements).

Sample	5ºC		25ºC	
	η_0/η_e	k x10^2 (s^{-1})	η_0/η_e	k x10^2 (s^{-1})
1	2.68	3.23	2.22	4.38
2	1.58	2.02	1.46	1.09
3	1.75	0.89	1.57	0.79
4	1.65	1.98	1.43	1.39
5	2.53	1.69	2.11	1.97
6	1.87	2.36	1.43	1.36
7	1.97	1.84	1.73	1.30
Stnd. Error	0.06812	0.0023	0.06812	0.0023

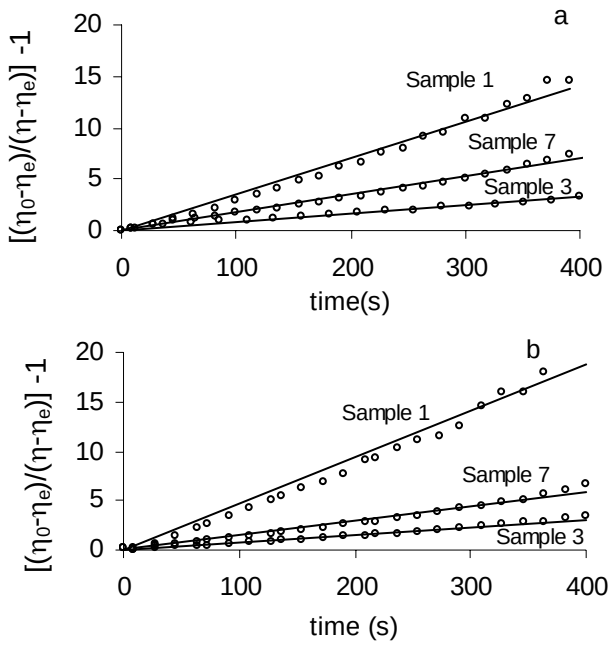

Figure 6. Testing of the second order structural kinetic model, Eq. (10), for some dairy dessert samples at 5ºC (a) and at 25ºC (b). Identification of samples in Table 1.

For both temperatures, sample 1 showed higher k values than the rest of samples, indicating faster rate of thixotropic breakdown, and a greater ratio of the initial to equilibrium viscosity (η_0/η_e), a relative measure of the extent of thixotropy (Table 2).

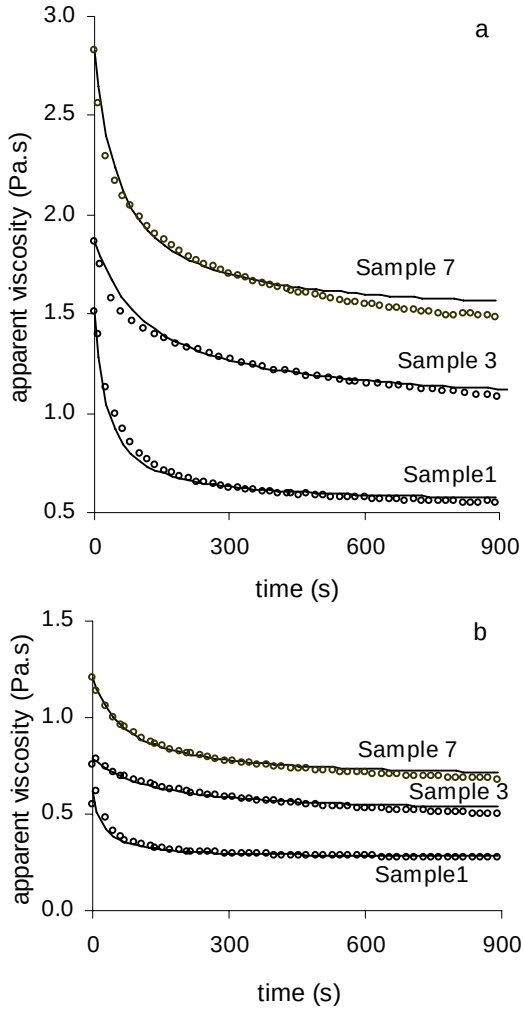

Figure 7. Apparent viscosity data at constant shear rate of 100s^{-1} for some dairy dessert samples at 5ºC (a) and at 25ºC (b). Experimental values (○) and fits to structural kinetic model (—). Identification of samples in Table 1.

The effect of temperature on η_0/η_e ratio was significant (F_t = 66.65, p= 0.000). For all samples, this ratio was lower at 25ºC. A significant sample-temperature interaction's effect (F_{int} = 5.46**,** p=0.004) on parameter k was found. The effect of temperature on k values was not the same for the different samples analysed: at 25ºC, the k values were higher for samples 1 and 5 and lower for the rest (Table 2). It seems like the structure responsible for time dependence in samples 1 and 5 was different from the others'. Nguyen et al. (1998) reported that k values for starch pastes increased or decreased with temperature depending on the type of starch and on the applied shear rate. Abu-Jdayil observed a decrease in k values with temperature in milled black cumin (2002) and an increase in milled sesame seeds (*tehineh*) (2003). More research is needed to analyse and identify the structural differences responsible for the effect of temperature on the rate of thixotropic breakdown.

3.2. Influence of temperature on steady flow behaviour

As reported in Section 2, a previous shearing of 5 minutes at 300 s^{-1} was applied to all samples to eliminate time dependence. On registering shear stress variation with shear rate, all samples showed non- Newtonian shear-thinning behaviour with an apparent initial resistance to flow. Experimental data fitted well to the Herschel-Bulkley model (Fig. 8) with R^2 values ranging between 0.993 and 0.998 for measurements at 5ºC and between 0.990 and 0.999 for those at 25ºC (Table 3).

The yield stress values, obtained for all samples at both temperatures, by fitting experimental data to the Casson model, were important - higher than 7.77 Pa at 5ºC and higher than 5.76 Pa at 25ºC (Table 3) - indicating plastic behaviour. The high yield stress values obtained suggest that, in spite of the possible effects of the rotor's inertia and of the friction forces generating in

concentric cylinders systems, the analysed samples have a real initial resistance to flow. Though these values were calculated by extrapolation, then being of an empirical rather than a rheological nature (Mewis & Spaull, 1976), their practical use in the characterisation of this type of products has been widely recognised (Costell et al., 1993).

Since the parameter K values depend on n values, apparent viscosity at 1 s^{-1} (η_1) values were used in the analysis of variance performed to study the effects of sample and temperature on flow properties. ANOVA results showed that sample-temperature interactions were significant for σ_0 (F_{int} = 5.40, p=0.005) and for η_1 (F_{int} = 6.63, p=0.002).

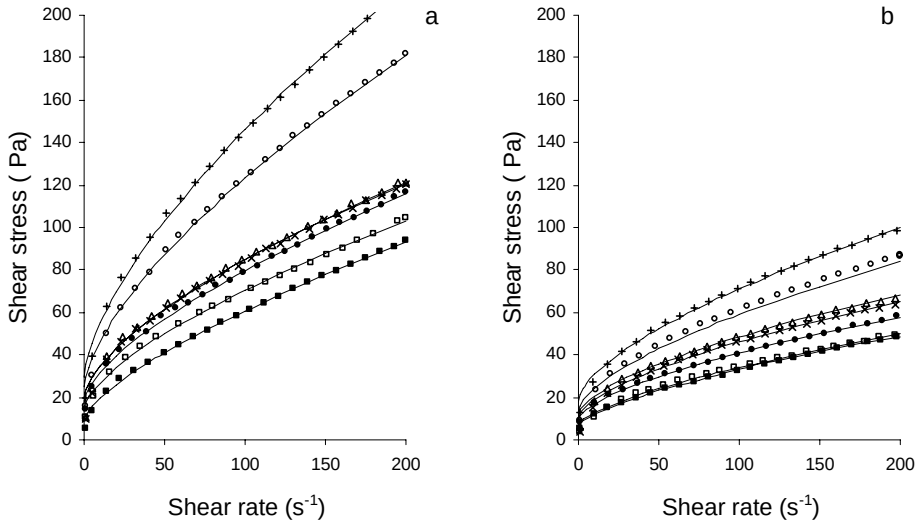

Figure 8. Equilibrium flow curves obtained for dairy dessert samples at 5ºC (a) and at 25ºC (b). Experimental values (■) 1, (□) 2, (●) 3, (○) 4, (×) 5, (▲) 6, (+) 7 and fits to Herschel-Bulkey model (—). Identification of samples in Table 1

Table 3. Herschel-Bulkley fit of natillas samples at 5ºC and at 25ºC (flow parameters values)[a b]

Sample	5ºC				25ºC			
	σ_0 (Pa)[c]	K (Pa.s^n)	n	η_{ap} (Pa.s)[d]	σ_0 (Pa)[c]	K (Pa.s^n)	n	η_{ap} (Pa.s^n)[d]
1	7.77	1.90	0.71	9.67	6.43	1.20	0.68	7.63
2	15.01	2.66	0.67	17.67	5.76	1.37	0.65	7.12
3	16.5	2.87	0.67	19.37	9.93	1.60	0.65	11.52
4	23.92	4.64	0.67	28.56	14.06	2.43	0.64	16.49
5	20.42	3.46	0.64	23.89	10.90	2.00	0.63	12.90
6	21.63	3.46	0.63	25.09	12.24	2.01	0.63	14.33
7	29.11	5.38	0.66	34.49	15.47	3.02	0.66	18.48
Stnd. Error	1.151	0.074	0.0058	1.18	1.151	0.074	0.0058	1.18

a. Average values of two measurements
b. $0.993 \leq R^2 \leq 0.998$ at 5ºC and $0.988 \leq R^2 \leq 0.999$ at 25ºC
c. Yield stress (σ_0) calculated by fitting experimental data to the Casson model ($\sigma^{0.5}=\sigma_0^{0.5}+K\gamma^{0.5}$)
d. Viscosity at 1 s^{-1}

Both yield stress and apparent viscosity values were lower at 25ºC, this difference being significant for all samples but for sample 1. The effect of temperature on flow index was significant but of low entity (Table 3). As reported for the parameters related to the time dependence properties, differences among samples for the flow parameters were always higher at 5ºC. At this temperature, sample 1 exhibited lower initial resistance to flow, lower consistency and lower pseudoplasticity than the rest of samples. As commented by Nayouf et al. (2003) for starch pastes, the differences in magnitude of the effect of temperature on the flow behaviour of different samples may be attributed mainly to the relative volume and deformability of starch granules. For the products analysed in this paper, these characteristics will, in turn, depend not only on the starch content of the

samples but also on the elaboration process conditions, mainly on the severity of the cooking process.

Similar results to those obtained here for “natillas” have been reported for starch pastes by other authors. Recently, Nayouf et al. (2003) studied the rheological properties of crosslinked waxy corn starch and concluded that, except for the lower concentration (2% starch) pastes, experimental data fitted well to the Herschel-Bulkley’s model. Acquarone and Rao (2003) also used this model to characterise the flow of waxy corn starch dispersions with added sucrose.

In summary, results obtained showed that, though quantitatively different, all samples of “natillas” behaved as time dependent fluids, whose variations with time fitted well to both the empirical Weltmann model and to the structural kinetics model proposed by Nguyen et al. (1998). After eliminating thixotropy by shearing, samples showed shear-thinning properties with measurable initial resistance to flow, e.g., a plastic behaviour that fitted well to the Herschel-Bulkley model. Although the extent of the differences varied among samples, in general, time dependence, plasticity and consistency were lower and pseudoplasticity was slightly higher at the higher temperature (25 vs. 5ºC).

Acknowledgements

We acknowledge the MCyT of Spain for financial support (Project AGL 2000-1590), and for the fellowship awarded to author Tárrega.

References

Abu-Jdayil, B. (2002). Rheology of milled black cumin. *Rheologica Acta*, 41, 441-447.

Abu-Jdayil, B. (2003). Modelling the time-dependent rheological beavior of semisolid foodstuffs. *Journal of Food Engineering*, 57, 97-102.

Acquarone , V. M., & Rao, M. A. (2003). Influence of sucrose on the rheology and granule size of cross-linked waxy maize starch dispersions heated at two temperatures. *Carbohydrate Polymers*, 51, 451-458.

Alloncle, M., & Doublier, J. L. (1991) Viscoelastic properties of maize starch/hydrocolloids pastes and gels. *Food Hydrocolloids*, 5, 455-467.

Barbosa-Cánovas, G. V., & Peleg, M. (1983). Flow parameters of selected commercial semi-liquid food products. *Journal of Texture Studies*, 14, 213-234.

Carbonell, E., Costell, E., & Durán, L. (1991a). Rheological behaviour of sheared jams. Relation with fruit content. *Journal of Texture Studies*, 22, 33-43.

Carbonell, E., Costell, E., & Durán, L. (1991b). Rheological indices of fruit content in jams: influence of formulation on time-dependent flow of sheared strawberry and peach jams. *Journal of Texture Studies*, 22, 457-471.

Cheng, D. C. H., & Evans, F. (1965). Phenomenological characterisation of the rheological behaviour of inelastic reversible thixotropic and antithixotropic fluids. *British Journal of Applied Physics*, 16, 599-617.

Costell, E. Carbonell, E., & Durán, L. (1993). Rheological indices of fruit content in jams: effect of formulation on flow plasticity of sheared strawberry and peach jams. *Journal of Texture Studies*, 24, 375-390.

Descamps, O., Langevin, P., & Combs, D.H. (1986). Physical Effect of stach/carrageenan interactions in water and milk. Food Technology, 40, 81-88.

Dolz, M., González, F., Delegido, J., Hernández, M. J., & Pellicer, J. (2000). A time-dependent expression for thixotropic areas. Application to aerosil 100 hydrogels. *Journal of Pharmaceutical Sciences*, 89, 790-797.

Hahn, S. J., Ree, T., & Eyring. (1959). Flow mechanism of thixotropic substances. *Industrial and Engineering Chemistry*, 51, 856-857.

Halmos, A. L., & Tiu, C. (1981). Liquid foodstuffs exhibiting yield stress and shear-degradability. *Journal of Texture Studies*, 12, 39-46.

Hernández. M. J. (1996). *Caracterización reológica de hidrogeles de MCC-NaCMC + almidón. Tixotropía y sinergismo*. Ph D Thesis. Universitat de València. Valencia, Spain.

Liu, H., & Eskin, N. A. M. (1998). Interactions of native and acetylated pea starch with yellow mustard mucilage, locust bean gum and gelatine. *Food Hydrocolloids*, 12, 37-41.

Longrée, K., Behaver, S., Buck, P., & Nowrey, J. E. (1966). Viscous behavior of custard systems. *Journal of Agriculture and Food Chemistry*, 14, 653-659.

Matser, A. M., & Steeneken, P. A. M. (1997). Rheological properties of highly cross-linked waxy maize starch in aqueous suspensions of skim milk components. Effects of the concentration of starch and skim milk components. *Carbohydrate Polymers*, 32, 297-305.

Mewis, J., & Spaull, A. J. B. (1976). Rheology of concentrated dispersions. *Advances in Colloid and Interface Science*, 6, 173-200.

Nadison, J., & Doreau, A. (1992). Carrageenan/starch interaction in cream desserts. In G. O. Phillips, P. A. Williams & D. J. Wedlock, *Gums and Stabilisers for the Food Industry 6* (pp. 287-295) Oxford University Press Ltd.

Nayouf, M., Loisel, C., & Doublier, J. L. (2003). Effect of thermomechanical treatment on the rheological properties of crosslinked waxy corn starch. *Journal of Food Engineering*, 59, 209-219.

Nguyen, Q. D., & Boger, D. V. (1985). Thixotropic behavior of concentrated bauxite residue suspensions. *Rheologica Acta*, 24, 427-437.

Nguyen, Q. D., Jensen, C. T. B., & Kristensen P. G. (1998). Experimental and modelling studies of the flow properties of maize and waxy maize starch pastes. *Chemical Engineering Journal*, 70, 165-171.

O'Donnell , H. J., & Butler, F. (2002). Time-dependent viscosity of stirred yogurt. Part I: couette flow. *Journal of Food Engineering*, 51, 249-254.

Paredes, M. D. C., Rao, M. A., & Bourne, M. C. (1989). Rheological characterization of salad dressings. 1. Steady shear, thixotropy and effect of temperature. *Journal of texute Studies*, 19, 247-258.

Skriver, A., Roemer, H., & Qvist, K. B. (1993). Rheological characterization of stirred yoghurt; viscometry. *Journal of Texture Studies*, 24, 185-198.

Tecante, A., & Doublier, J. L.(1999). Steady flow and viscoelastic behavior of crosslinked waxy cornstarch-k-carrageenan pastes and gels. *Carbohydrate Polymers*, 40, 221-231.

Thebaudin, J. Y., Lefebvre, A. C., & Doublier, J. L (1998). Rheology of starch pastes from starches of different origins: Aplications to starch-

based sauces. *Lebensmitttel Wissenschaft und Thecnologie*, 31, 354-360

Tiu, C., & Boger, D. V. (1974). Complete rheological characterization of time dependent food products. *Journal of Texture Studies*, 5, 329-338.

Umadevi, S., & Raghavendra, M. R. (1987). Effect of hydrocolloids on the rheological properties of wheat starch. *Carbohydrate Polymers*, 7, 395-402.

Weltmann, R. N. (1943). Breakdown of thixotropic structure as function of time. *Journal of Applied Physics*, 14, 343-350.

Wijk, R. A., van Gemert, L. J., Terpstra, M. E. J., & Wilkinson, C. L.(2003). Texture of semi-solids; sensory and instrumental measuraments on vanilla custard desserts. *Food Quality and Preference*, 14, 305-307

Wischmann, B., Norsker, M., & Adler-Nissen, J. (2002). Food product models developed to evaluate starch as food ingredient. *Nahrung/ Food*, 46, 167-173.

RHEOLOGICAL CHARACTERIZATION OF SEMISOLID DAIRY DESSERTS. EFFECT OF TEMPERATURE*

A. Tárrega, L. Durán & E. Costell **

Instituto de Agroquímica y Tecnología de Alimentos. CSIC.
P.O. Box 73. 46100 Burjassot (Valencia). Spain.

Abstract

The rheological behaviour of seven samples of commercial Spanish dairy dessert "natillas" were studied by both static and dynamic methods and the influence of the usual consumption temperatures (5 and 25ºC) on both their flow and their viscoelastic properties was analysed. All samples exhibited typical shear thinning behaviour, the flow curves fitting well to the Carreau model. As expected, data obtained at 25ºC followed the same pattern but with lower apparent viscosity values than those at 5ºC. The mechanical spectra obtained for most samples was typical of gelled materials, at both temperatures, with G' higher than G'', both moduli showing little variation with frequency. All samples showed increasing tan δ values with frequency, indicating a higher contribution of the viscous component at higher frequencies. The differences in rheological behaviour between samples, obtained by static shear and by oscillatory shear measurements, were highly coincident.

Keywords: Flow behaviour, Viscoelasticity, Dairy desserts, Shear thinning, Carreau model, Cox-Merz rule

---

* Part of this paper was presented as a poster at "The Twelfth Gums and Stabilisers for the Food Industry Conference", Wrexham, June 24-27, 2003

**Corresponding author. Tel.:+34-96-3900022; Fax: +34-96-3636301.
E-mail address: ecostell@iata.csic.es

1. Introduction

The “natillas”, semisolid dairy dessert of wide consumption in Spain, is composed of milk, starch, hydrocolloids, sugars, colorants and aromas. Similar products can be found in several European countries like “Crème dessert” in France, “Vanilla vla” in The Netherlands or “ Vanilla custard dessert” in the United Kingdom, though with notable differences in composition and physical properties. The rheological and sensory properties of this group of products are strongly influenced by the particular characteristics of some ingredients, like fat content of milk, type of starch, and/or type and concentration of hydrocolloids, and their crossed interactions.(Nadison & Doreau, 1992; Descamps, Langevin & Combs, 1986; De Wijk, Rasing & Wilkinson, 2003 & Weenen, Gemert, Van Doorn, Dijksterhuis & De Wijk, 2003). Wide information can be found in the literature on the rheological behaviour of starch pastes and on the changes produced by adding different types of hydrocolloids (Umadevi & Raghavendra, 1987; Alloncle & Doublier, 1991; Abdulmola, Hember, Richardson & Morris, 1996; Mandala & Bayas, 2003; Liu & Skin, 1998), on the interactions between several hydrocolloids and milk (Dickinson, 1998; Syrbe, Bauer & Klostermeyer, 1998; Rodd, Davis, Dunstan, Forrest & Boger, 2000) as well as on the effects produced by substituting milk for water in starch pastes (Matser & Steeneken, 1997). However, only a few papers deal with the rheological characterisation of commercial dairy desserts or their corresponding model systems.Wischmann, Norsker & Adler-Nissen (2002) studied the effects of starch concentration in dairy dessert model systems, which showed time dependent and pseudoplastic flow and viscoelastic properties typical of structured gels. Depypere, Verbeken, Thas & Dewettinck (2003) studied the interactions between κ-carrageenan, corn starch and dairy proteins and analysed the viscoelastic properties of dairy model systems. Batista, Nunes & Sousa (2002)

characterised both the flow and the viscoelasticity of two commercial dairy desserts, as affected by the substitution of vegetable proteins for milk.

Flow curves of structured or pseudoplastic fluids, obtained along a wide range of shear rates, showed an initial region with constant apparent viscosity (η_0), followed by a region where η values decreased exponentially (a straight line in logarithmic coordinates). At very high shear rates a second region with constant apparent viscosity (η_∞) could be observed (Barnes, 2000). One of the most accepted models for describing this type of flow behaviour is the Carreau model, applied to characterise the flow of starch pastes (Chamberlain & Rao, 1999) and of dairy desserts (Batista et al, 2002).

Concerning the use of oscillatory methods, frequency sweeps are the most frequently used to follow the changes in both the viscous and the elastic components with frequency on applying a certain shear stress or shear rate. The result obtained is considered to be the "fingerprint" of the analysed product and is commonly used to compare the effects of different ingredients or processing conditions on the material's viscoelastic properties (Steffe, 1996). Cox & Merz (1958) observed that the complex viscosity (η^*) values were very similar to the apparent viscosity (η_{ap}) values at equal values of frequency and shear rate:

$$\eta^* = \eta_{ap}\,|_{\omega=\dot{\gamma}} \qquad (1)$$

However, Bistany & Kokini (1983a,b) reported that this rule was not valid for a wide variety of fluid and semisolid foods, for which they obtained complex viscosity values notably higher than the apparent viscosity values.

They proposed a non-linear modification of the Cox-Merz rule, by which both parameters can be empirically related:

$$\eta^* = K \cdot \eta_{ap}{}^{\alpha}|_{\omega=\dot{\gamma}} \qquad (2)$$

where K and α are experimental constants.

Several authors have studied the validity of the Cox-Merz rule in starch pastes with not always concordant results. Roberts & Cameron (2002) found that this rule holds in potato starch pastes at different starch concentrations. Chamberlain et al. (1999) reported this to apply in slightly branched corn starch (45 and 90 min acid converted starch) pastes but not in more branched (0 and 25 min acid converted starch) starch pastes of the same origin, where the complex viscosity values were lower than those of the apparent viscosity. Moreover, Han, Campanella, Guan, Keeling, & Hamaker (2002) observed that in normal corn starch η^* values were much higher than η_{ap} ones while in waxy corn starch the opposite was true. Of great interest are the results obtained by Rao & Tattiyakul (1999), who found that the Cox Merz rule could not be applied in 4% tapioca starch pastes but the sought relation between both viscosities could be described by the above mentioned modified Cox Merz rule.

The objective of this work was to characterise the rheological behaviour of Spanish commercial "natillas" by both static and dynamic methods and to analyse the influence of the usual consumption temperatures (5 and 25ºC) on both their flow and their viscoelastic properties.

2. Materials and methods

2.1. Samples

Seven samples of vanilla dairy dessert (*natillas*) of different brands and characteristics, covering the commercial range, were purchased from the local market (Table 1). The samples were stored at 4±1ºC prior to testing and all measurements were performed within the declared shelf-life period of each sample.

Table 1. Main composition and price level of commercial vanilla cream dairy desserts samples.

Sample	Dairy ingredients [a]	Thickeners [a]	pH [b]	Soluble solids [b] (º Brix)	Price[c]
1	Semi-skimmed milk	Modified starch Carrageenan Xanthan gum	6.81	24.5	1.4
2	Milk Semi-skimmed milk	Modified starch Carrageenan Guar gum	6.76	23.7	1
3	Milk Cream Semi-skimmed milk powder	Acetylated distarch adipate Gelatine	6.61	28.3	2.3
4	Milk Cream Dairy solids	Modified starch Carrageenan Fatty acid esters	6.60	26.3	2.5
5	Milk Cream	Modified starch Carrageenan Guar gum	6.76	23.5	2.5
6	Milk Cream	Modified starch Carrageenan Guar gum	6.72	24.5	1.7
7	Milk Cream Dairy solids	Modified starch Carrageenan Fatty acid esters	6.75	24.5	1.9

a. Declared in label.
b. Average value of two measurements
c. Lower price considered as reference unit

2.2. Rheological measurements

The rheological behaviour of vanilla dairy dessert samples was characterised using steady shear and oscillatory shear measurements. All measurements were carried out in a controlled stress rheometer (RheoStress 1, Karslruhe, Germany), monitored by a Rheowin Projob Manager, using a serrated parallel plates sensor system (6 cm diameter and 1mm gap) to avoid wall slip phenomena. A glass solvent trap was used to prevent water evaporation. All measurements were made at two temperatures: 5 ± 0.5 and 25 ± 0.5 ºC, selected as representative of the usual consumption temperatures. At least two replicates of each measurement were made.

2.2.1. Steady shear data

Flow curves were obtained from stepped shear stress ramp (steady state approximation: 5 min per point) from 0.5 to 100 Pa for all samples except for sample 1 (0.05- 100 Pa) and sample 2 (0.1 – 100 Pa). Corrections of the shear stress data, accounting for the use of a plate-plate system, were made. Using SPSS programme data were fitted to the Carreau model:

$$\eta_{ap} = \eta_\infty + (\eta_0 - \eta_\infty)/(1 + (\dot{\gamma} / \dot{\gamma}_c)^2)^m \qquad (3)$$

where η_0 (Pa.s) is the limit viscosity at low shear rates, η_∞ (Pa.s) is the limit viscosity at high shear rates, $\dot{\gamma}_c$ (s^{-1}) is the critical shear rate at the start of the pseudoplastic region and m is a parameter related to the slope of the latter region.

2.2.2. Small amplitude oscillatory shear data

To determine the linear viscoelastic region stress sweeps were run at 1 Hz. Frequency sweeps were performed over the range f = 0.01-10 Hz and the values of G', G'', tan δ and η*, as a function of frequency, were calculated using Rheowin Data Manager Software.

The validity of the Cox-Merz rule (eq.1) was studied for each sample and temperature by comparing the experimental values of η_{ap} versus $\dot{\gamma}$ and those of η* versus ω in a double logarithmic plot. The relationship between apparent and complex viscosities was analysed with the modified Cox-Merz rule (eq.2).

2.3. Statistical analysis

The effect of temperature on the values of the Carreau model parameters was studied by a two factors (sample and temperature) analysis of variance with

interaction. The Fisher test (α=0.05) was used to calculate the minimum significant differences. Calculations were carried out with the Statgraphics Plus 3.1 programme.

3. Results

3.1. Steady shear data

The flow curves of all samples of vanilla dessert exhibited a typical shear thinning behaviour with constant zero shear rate viscosity. All samples showed rather similar flow curves except sample 1, whose viscosity values were clearly lower at both temperatures and more so in the Newtonian region. As expected, data obtained at 25ºC followed the same pattern but with lower apparent viscosity values than those at 5ºC. Flow curves for samples 1, 2, 4 and 6 are shown in Figure 1.

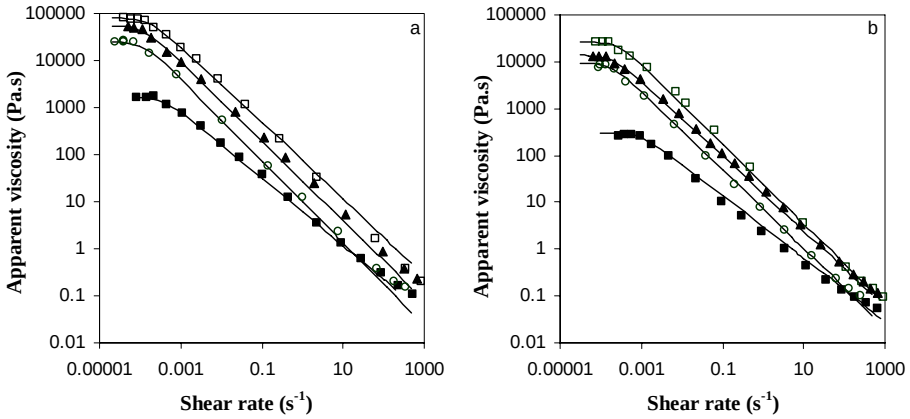

Figure 1. Steady shear flow curves at 5ºC (a) and at 25 ºC (b) for vanilla dairy dessert samples: 1(■), 2 (○), 4 (▲) and 6 (□) and fits to Carreau model (—). Identification of samples in table 1.

The Carreau model, originally included four parameters (eq. 3), but in this case, for some samples, negative values were obtained for parameter η_∞ , most likely due to the lack of data at high shear rates in the region of the limiting viscosity. This kind of problem was found by Chamberlain et al (1999) for starch pastes and Lopes da Silva, Goçalves & Rao (1992) for pectin and locust bean gum, because $\eta_{ap} >> \eta_{\infty.}$ Both of them proposed using a simplified Carreau model (4) with only three parameters ($\eta_\infty \approx 0$).

$$\eta_{ap} = \eta_0 / (1 + (\dot{\gamma} / \dot{\gamma}_c)^2)^m \qquad (4)$$

Data of "natillas" samples fitted relatively well (R^2 values between 0.977 and 0.998) to the simplified Carreau model (Table 2). Differences in this model parameters' values were observed among samples, the main ones being the much lower Newtonian viscosity (η_0), the higher critical shear rate values and the reduced pseudoplastic character (lower m values) shown by sample 1. It can then be stated that the latter sample presented less resistance to flow but more stability under the effect of shear since the reduction of viscosity took place at higher shear rates and was less pronounced.

Table 2. Carreau model fitting data for vanilla dairy dessert samples at 5ºC and at 25ºC[a,b]. Identification of samples in table 1.

Samples	5ºC			25ºC		
	η_0 (Pa.s)	γ_c (s^{-1})	m	η_0 (Pa.s)	γ_c (s^{-1})	m
1	2102	$3.5 \cdot 10^{-4}$	0.37	353	$8.2 \cdot 10^{-4}$	0.33
2	24133	$1.1 \cdot 10^{-4}$	0.42	8266	$1.8 \cdot 10^{-4}$	0.42
3	43133	$1.8 \cdot 10^{-4}$	0.41	19791	$2.2 \cdot 10^{-4}$	0.43
4	58456	$1.2 \cdot 10^{-4}$	0.43	14488	$1.9 \cdot 10^{-4}$	0.40
5	78699	$1.7 \cdot 10^{-4}$	0.40	34910	$3.0 \cdot 10^{-4}$	0.41
6	77369	$1.6 \cdot 10^{-4}$	0.40	27892	$2.8 \cdot 10^{-4}$	0.41
7	58265	$2.0 \cdot 10^{-4}$	0.43	16175	$2.0 \cdot 10^{-4}$	0.40

[a] Average values of two measurements
[b] $0.978 \leq R^2 \leq 0.996$ at 5ºC and $0.977 \leq R^2 \leq 0.998$ at 25ºC

The effect of the sample-temperature interaction on the Carreau model parameters values was significant (F_{int} = 6.86, p= 0.0015, for $\eta_{0;}$ F_{int} = 2.88, p= 0.0481, for $\dot{\gamma}_c$ and F_{int} = 6.66, p= 0.0017, for m), which means that the effect of temperature on all three parameters was different for the various analysed samples. The most affected parameter was $\eta_{0,}$ shown to be lower at the higher temperature in all cases. For sample 1, however such difference was not significant (α=0.05). Parameter $\dot{\gamma}_c$ values were higher at 25ºC ($8.2 \cdot 10^{-4}$ s^{-1}) than at 5ºC ($3.5 \cdot 10^{-4}$ s^{-1}) only for sample 1. Finally, parameter m values were lower at 25ºC for samples 1, 4 and 7.

3.2. Dynamic rheological data

The linear viscoelastic region, defined in previous stress sweeps, was found to be somewhat wider at 5ºC (up to about 1 Pa) than at 25ºC (up to about 0.3 Pa). Frequency sweeps were then run at 0.1 Pa. Coincident with the results shown above for the obtained flow curves, the behaviour of sample 1 under oscillatory shear was very different from that of the rest of samples. The mechanical spectra obtained for most samples was typical of gelled materials with G' values higher than G'' ones and both showing little variation with frequency. Sample 1 showed much lower G' and G'' values, both depending on frequency: G' was over G'' at low frequencies but of the same magnitude at high frequencies, indicating a much weaker gel structure (Figure 2). All samples showed increasing tan δ values with frequency, that is, a higher contribution of the viscous component at higher frequencies (Figure 3). In order to study the effect of temperature, G', G'', tan δ and η^* values were determined at a frequency of 1 Hz. Values of G' and G'' were lower at 25ºC (Table 3) but the differences found varied depending on samples.

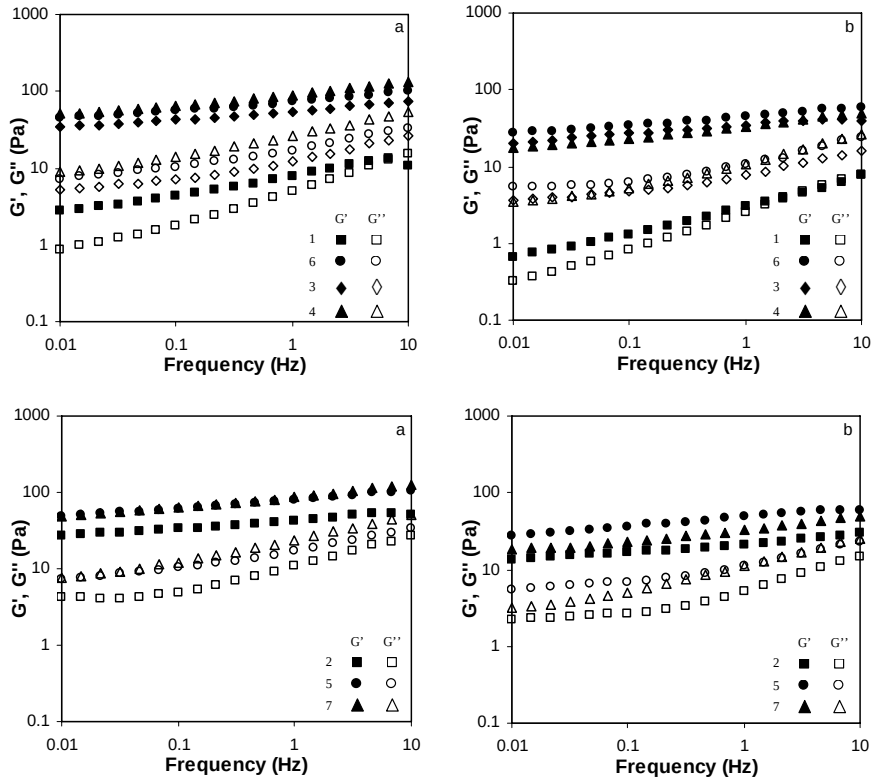

Figure 2. Mechanical spectra for vanilla dairy dessert samples at 5ºC (a) and at 25ºC (b) in the linear domain (σ=0.1 Pa). Identification of samples in table 1.

Considering tan δ and η∗ values at 1 Hz, two groups of samples could be distinguished as to the effect of temperature on their response. In one group (samples 2, 3, 5, and 6) tan δ values were practically the same at both temperatures while in the other group (samples 1, 4, and 7) they were higher at 25º C (Figure 4). In the latter group the observed increase in η∗ values was relatively larger than in the samples of the former group (Figure 5). These results show that the structure of samples 1, 4, and 7 was more sensitive to temperature changes than that of the rest of samples. Their viscous component was clearly higher and the decrease in complex viscosity with temperature more pronounced.

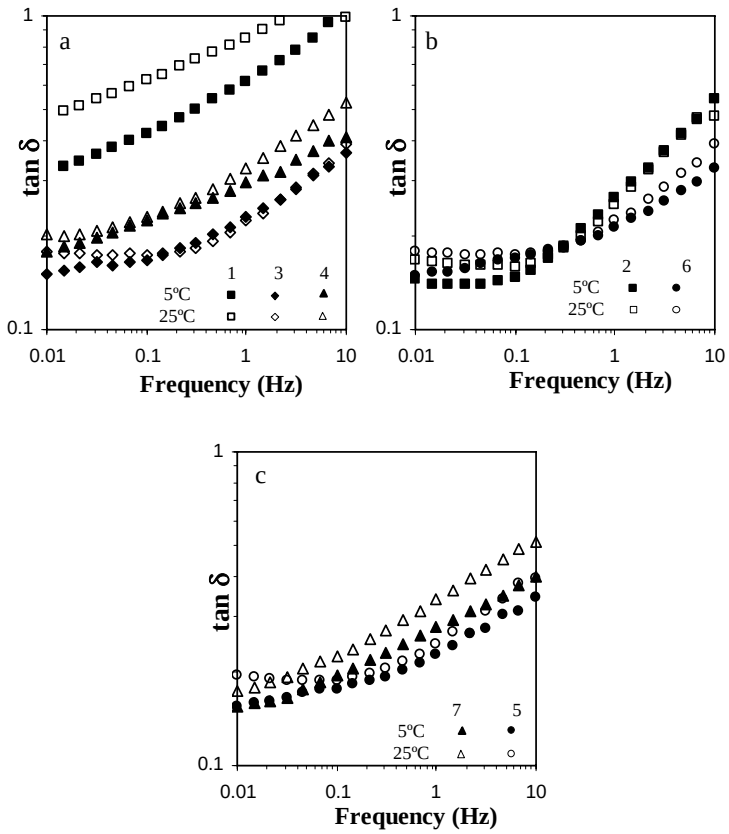

Figure 3. Variation of tan δ with frequency at 25ºC and at 5ºC for vanilla dairy dessert samples. (a) samples 1, 3 & 4, (b) samples 2 & 6 and (c) samples 5 & 7. Identification of samples in table 1.

The differences in rheological behaviour among samples, obtained by static shear and by oscillatory shear measurements, were highly coincident: Sample 1 was clearly different from the rest. Samples 2 and 3 showed an intermediate type of behaviour. The similarity found in the Carreau η_0, $\dot{\gamma}_c$, and m values between samples 4 and 7 or between samples 5 and 6 could also be observed in both the G' and G'' values.

Table 3. Storage modulus (G') and loss modulus (G'') values at 1 Hz for vanilla dairy dessert samples [a]. Identification of samples in table 1.

Sample	5ºC		25ºC	
	G' (Pa)	G'' (Pa)	G' (Pa)	G'' (Pa)
1	8.1	5.0	3.0	2.5
2	37.6	9.7	19.9	5.1
3	50.3	11.6	35.4	7.9
4	87.1	25.6	35.8	11.7
5	82.2	17.3	51.3	11.1
6	71.7	16.2	52.6	11.8
7	88.8	24.4	31.0	10.7

[a] Average values of two measurements

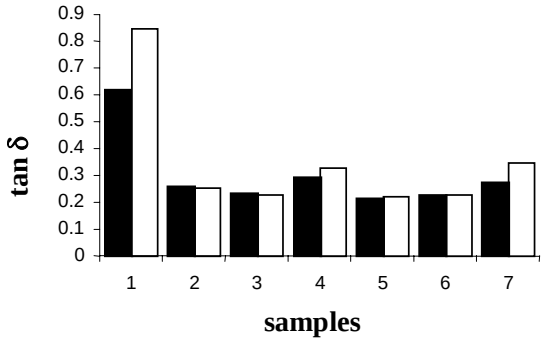

Figure 4. Values of tan δ at 1 Hz, at 5ºC (■) and at 25ºC (□). Identification of samples in table 1.

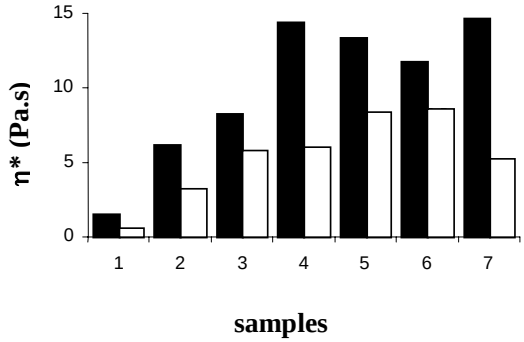

Figure 5. Values of complex viscosity at 1Hz, at 5ºC (■) and at 25ºC (□). Identification of samples in table 1.

3.3. Cox-Merz rule

When plots of apparent viscosity (η_{ap}) values versus shear rate ($\dot{\gamma}$) and those of complex viscosity ($\eta*$) versus frequency (ω) coincide, the Cox-Merz rule applies. This has been found to be true for samples 1, 5, and 6, while for the rest of samples η_{ap} values were lower than those of η^* (Figure 6).

The suitability of the modified Cox-Merz rule was studied by fitting both the variation of η_{ap} with $\dot{\gamma}$ and the variation of η^* with ω to the power law. Then the relationship between η_{ap} and η^* was analysed by the modified Cox-Merz rule (Table 4).

Table 4. Power law parameters for η_{ap} versus $\dot{\gamma}$ and $\eta*$ versus ω and modified Cox-Merz rule parameters for vanilla dairy desserts. Identification of samples in table 1.

Sample	Temperature ºC	Steady shear $\eta_{ao} = A \cdot \dot{\gamma}^a$		Oscillatory $\eta^* = B \cdot \omega^b$		mod. Cox-Merz $\eta^* = K \cdot \eta_{ap}^{\alpha}$	
		A	a	B	b	K	α
1	5ºC	6.74	0.68	5.97	0.71	0.82	1.04
	25ºC	2.47	0.67	1.96	0.61	0.92	0.90
2	5ºC	13.14	0.80	28.10	0.89	1.63	1.11
	25ºC	6.68	0.77	18.15	0.88	2.10	1.13
3	5ºC	32.30	0.81	46.00	0.88	1.63	1.10
	25ºC	17.04	0.81	28.73	0.88	1.31	1.09
4	5ºC	37.35	0.79	68.00	0.84	1.44	1.06
	25ºC	16.38	0.80	26.28	0.83	1.44	1.04
5	5ºC	59.22	0.86	70.89	0.89	1.03	1.04
	25ºC	35.59	0.84	39.64	0.88	0.93	1.05
6	5ºC	61.22	0.85	60.77	0.89	0.83	1.04
	25ºC	27.523	0.94	37.26	0.88	1.16	1.05
7	5ºC	43.14	0.82	75.02	0.86	1.47	1.05
	25ºC	17.88	0.80	26.23	0.84	1.27	1.05

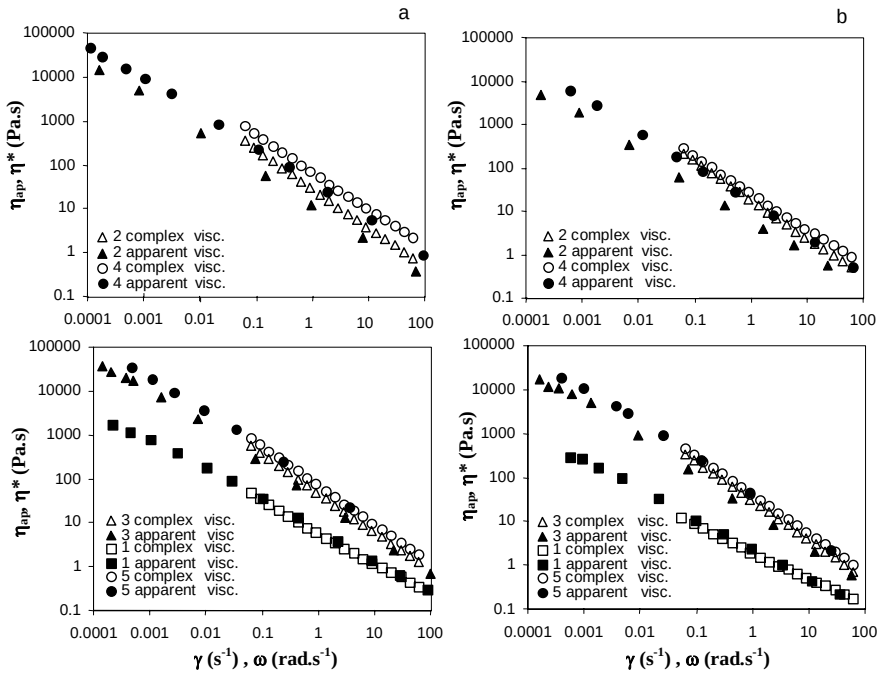

Figure 6. Cox-Merz plot for vanilla dairy dessert samples at 5ºC (a) and at 25ºC(b). Identification of samples in table 1.

The observations made graphically from Figure 6 plots were confirmed by the modified Cox-Merz rule parameters' values: for samples 1, 5, and 6, K and α values were closer to 1 (0.82 - 1.16 and 0.9 - 1.05, respectively), than for the rest of samples (1.27 - 2.10 and 1.04-1.13, respectively). According to some authors (Rao, Okechuckeu, Da Silva & Oliveira, 1997), deviation from the Cox-Merz rule indicates a gel-like structure. However, in our case in samples 5 and 6 the Cox-Merz rule held but their mechanical spectra showed the characteristics of a type of structure of similar or even higher lever of gelling than that of samples 2, 3, 4, and 7. The latter ones, in contrast, showed deviation from this rule.

The particular rheological behaviour of crosslinked starch, presumably present in the analysed commercial samples, could perhaps be responsible for the different behaviour as to the Cox-Merz rule fitting results.

Acknowledgements

To MCyT of Spain for financial support (Projects AGL 2000-1590 and AGL 2003-0052) and for the fellowship awarded to author Tárrega.

References

Abdulmola, N. A., Hember, M. W. N., Richardson R. K. & Morris E. R. (1996). Effect of xanthan on the small-deformation rheology of crosslinked and uncrosslinked waxy maize starch. *Carbohydrate Polymers*, 31, 65-78.

Alloncle, M. & Doublier, J. L. (1991) Viscoelastic properties of maize starch/hydrocolloids pastes and gels. *Food Hydrocolloids*, 5, 455-467.

Barnes, H.A. (2000). A handbook of elementary rheology. Aberystwyth: Institute of Non-Newtonian Fluid Mechanics, University of Wales.

Batista, P., Nunes, M. C. & Sousa, I. (2002). Physical characterisation of commercial dairy desserts. In F.J.Martínez Boza, A. Guerrero, P.Partal, J.M. Franco & J. Muñoz., *Progress in Rheology Theory and Applications* (pp. 449-452). Sevilla: Publicaciones Digitales S.A.

Bistany, K. L. & Kokini, J. L. (1983a). Comparison of steady shear rheological properties and small amplitude dynamic viscoelastic properties of fluid food materials. *Journal of Texture Studies*, 14, 113-124.

Bistany, K. L. & Kokini, J. L. (1983b). Dynamic viscoelastic properties of foods in texture control. *Journal of Rheology*, 27, 605-620.

Chamberlain, E. K. & Rao, M. A. (1999). Rheological properties of acid converted waxy maize starches in water 90% DMSO/10% water. *Carbohydrate Polymers*, 40, 251-260.

Cox, W. P. & Merz E. H. (1958). Correlation of dynamic and steady flow viscosities. *Journal of Polymer Science*, 28, 619-622.

De Wijk, R. A., Rasing, F. & Wilkinson, C. L. (2003). Texture of semi-solid: sensory flavor-texture interactions for custard desserts. *Journal of Texture Studies*, 34, 131-146.

Depypere, F., Verbeken, D., Thas, O. & Dewettinck, K. (2003). Mixture design approach on the dynamic rheological and uniaxial compression behaviour of milk desserts. *Food Hydrocolloids*, 17, 311-320.

Descamps, O., Langevin, P. & Combs, D.H. (1986). Physical Effect of starch/carrageenan interactions in water and milk. *Food Technology*, 40, 81-88.

Dickinson E. (1998). Stability and rheological implications of electrostatic milk protein-polysaccharide interactions. *Trends in Food Science and Technology*, 9, 347-354.

Han, X. Z., Campanella, O. H., Guan, H., Keeling, P.L. & Hamaker, B. R. (2002). Influence of starch granule associated protein on the rheological properties of starch pastes. Part II. Dynamic measurements of viscoelastic properties of starch pastes. *Carbohydrate Polymers*, 49, 323-330.

Liu, H. & Eskin, N. A. M. (1998). Interactions of native and acetylated pea starch with yellow mustard mucilage, locust bean gum and gelatine. *Food Hydrocolloids*, 12, 37-41.

Lopes Da Silva, J. A., Gonçalves, M. P. & Rao, M. A. (1992).Rheological properties of high-methoxyl pectin and locust bean gum solutions in steady shear. *Journal of Science*, 57, 443-448.

Mandala I. G. & Bayas E. (2003). Xanthan effect on swelling, solubility and viscosity of wheat starch dispersions, *Food Hydrocolloids*, (in press).

Matser, A. M. & Steeneken, P. A. M. (1997). Rheological properties of highly cross-linked waxy maize starch in aqueous suspensions of skim milk components. Effects of the concentration of starch and skim milk components. *Carbohydrate Polymers*, 32, 297-305.

Nadison, J. & Doreau, A. (1989). Carrageenan/starch interaction in cream desserts. En "F.I.E. Food ingredients Europe. Conference Proceedings 1989. Paris 27-29 September 1989". Maarssen, Netherlands; ISBN 90-73220-01-7.

Rao, M. A. & Tattiyakul, J. (1999). Granule size and rheological behavior of heated tapioca starch dispersions. *Carbohydrate Polymers*, 38, 123-132.

Rao, M.A., Okechukwu, P.E, Da Silva P.M.S. & Oliveira, J.C. (1997). Rheological behavior of heated starch dispersions in excess water: role of starch granule. *Carbohydrate Polymers* 33, 273–283.

Roberts, S. A., & Cameron, R. E. (2002). The effects of concentration and sodium hydroxide on the rheological properties of potato starch gelatinisation. *Carbohydrate Polymers* 50, 133–143.

Rodd, A. B., Davis, C. R., Dunstan, D. E., Forrest B. A. & Boger, D. V. (2000) Rheological characterisation of weak gel carrageenan stabilised milks. *Food Hydrocolloids*, 14, 445-454.

Steffe, J. F.(1996) Rheological methods in Food Process Engineering, 2nd ed., p. 158-254, Freeman Press, East Lansing, Michigan.

Syrbe, A., Bauer, W. J. & Klostermeyer, H. (1998). Polymer science concepts in diry systems- An overview of milk protein and food hydrocolloid interaction. *International Dairy Journal*, 8, 179-193.

Umadevi, S. & Raghavendra, M. R. (1987). Effect of hydrocolloids on the rheological properties of wheat starch. *Carbohydrate Polymers*, 7, 395-402.

Weenen, H., Van Gemert, J. L., Van Doorn, J. M., Dijksterhuis, G. B. and De Wijk, R. A. (2003). Texture and mouthfeel of semisolid foods: comercial mayonnaises, dressings, custard desserts and warm sauces. *Journal of Texture Studies*, 34, 131-146.

Wischmann, B., Norsker, M. & Adler-Nissen, J. (2002). Food product models developed to evaluate starch as food ingredient. *Nahrung/ Food*, 46, 167-173.

COLOUR AND CONSISTENCY OF SEMI-SOLID DAIRY DESSERTS. INSTRUMENTAL AND SENSORY MEASUREMENTS

A. Tárrega & E. Costell*

Instituto de Agroquímica y Tecnología de Alimentos. CSIC.

P.O. Box 73. 46100 Burjassot (Valencia). Spain.

Abstract

Colour and consistency of seven commercial samples of vanilla dairy desserts were studied. All samples showed the typical spectral curve for yellow-orange coloured materials, with maximum reflectance values at wavelengths over around 550 nm. Significant differences between samples in the value of the colour parameters were found. Flow behaviour of samples was characterised as time dependent and shear thinning. Data from the upward flow curve were fitted to the Herschel-Bulkley model and the values of yield stress (σ_0), flow index (n), and apparent viscosity at 10 s^{-1} (η_{10}) were obtained. From the oscillatory rheological measurements, values of storage modulus (G'), loss modulus (G''), loss angle tangent (tan δ) and complex viscosity ($\eta*$) were determined. Significant differences in all rheological parameters were detected between samples. Sensory ranking tests were performed by 42 assessors to evaluate perceptible differences in the colour and in the consistency of the samples. Correlations between sensory and instrumental data were determined using the Spearman correlation coefficient. Results showed a significant positive correlation between sensory colour and parameter a*(red component) and significant negative correlations with parameters L* (brightness) and h* (hue). Oral thickness showed the best correlation with yield stress from the flow parameters and with the storage modulus at 1 Hz and complex viscosity at 7.95 Hz (50 $rad.s^{-1}$) from the viscoelastic parameters.

Keywords: Dairy desserts, colour, thickness, sensory evaluation, rheological measurements

*Corresponding author. Tel.:+34-96-3900022; Fax: +34-96-3636301.
E-mail adress: ecostell@iata.csic.es

1. Introduction

Semisolid dairy desserts of different flavours are of wide consumption in Europe. Their nutritional and sensory characteristics favour their consumption by several groups of consumers like children or elder people. Vanilla flavoured products ("Natillas" in Spain, "Vanilla vla" in The Netherlands or "Crème dessert" in France), are the most popular ones. Basically they are formulated with milk, thickeners (starch and hydrocolloids), sucrose, vanilla aroma, and colorants. The characteristics of these ingredients- fat content of milk, type and concentration of starch, type and concentration of hydrocolloid, aroma and colorant- and their crossed interactions should produce noticeable differences in the physical and sensory properties of the formulated products and these differences could influence the consumer acceptance.

Some literature references can be found reporting the effect of some ingredients on textural properties and rheological behaviour and on the effect of flavour-texture interactions in model dairy desserts. Parker and Tilly (1994) analysed the influence of ί-carrageenan on thixotropy of dairy desserts and de Vries (2002) studied the effect of different types of carrageenan on the breaking strength of starch-milk systems. Wischmann, Norsker and Adler-Nissen (2002) studied the effects of starch concentration on both flow behaviour and viscoelasticity of dairy cream model systems and observed that they all showed time-dependent and pseudoplastic flow and that their viscoelastic nature was due to a gelled structure. Depeyre, Verbeken, Thas and Dewettinck (2003) studied the effect of interactions between κ-carrageenan, corn starch and dairy proteins on the viscoelastic properties and on the compression resistance of model systems. Possible interactions between flavour and texture perception in custard desserts model systems were investigated by De Wijk, Rasing and Wilkinson (2003). These

authors studied the effects of four flavorants (diacetyl, benzaldehyde, vanillin and caffeine) on perceived odour, flavour and texture and on the rheological behaviour of vanilla desserts. They concluded that the flavorants added affected odour and flavour ratings and that three of them, affected the structure of model systems, which resulted in changes in perceived thickness, creaminess and fattiness. Lethuaut, Brossard, Rouseau, Bousseau and Genot (2003) studied the effect of sucrose concentration and the carrageenan type on mechanical and texture assessment of vanilla dairy desserts as well as the impact of texture variation on sweetness perception. They observed that the firmness of κ- and λ-carrageenan desserts, the springiness of í-carrageenan desserts and the unctuousness of λ-carrageenean desserts increased with sucrose concentration and that the carrageenan type influenced sweetness perception. However, only a few papers deal with rheological or sensory characterization of commercial vanilla dairy desserts and there is no information about the possible relationships between differences on instrumental measures of physical properties of these products and changes in their sensory characteristics. Batista, Nunes and Sousa (2002) characterised both the flow and the viscoelasticity of two commercial dairy desserts as affected by the substitution of vegetable proteins for milk and Tárrega, Durán and Costell (2004 and 2005) studied the influence of the usual consumption temperatures (5 and 25ºC) on the flow and the viscoelasticity of seven Spanish commercial samples of "natillas". All samples showed flow time dependence and shear thinning behaviour and for most of them the mechanical spectra obtained was typical of gelled materials. De Wijk, van Gemert, Terpstra and Wilkinson (2003) used a Quantitative Descriptive Analysis to investigate the sensory properties of twelve commercial Dutch vanilla custard desserts, including dairy and non-dairy samples. In the resulting sensory space two main sensory dimensions, one running from melting to thick and another one running from rough to creamy-soft, could be recognised.

The aims of this work were to analyse the variations in colour and consistency of commercial samples of Spanish "natillas" and the relationships between instrumental and sensory measurements.

2. Materials and Methods

2.1. Samples

Seven samples of vanilla dairy dessert (*natillas*) of different brands and characteristics, covering the commercial range, were purchased from the local market (Table 1). The samples were stored at 4±1ºC prior to testing and all measurements were performed within the declared shelf-life period of each sample.

Table 1. Main composition and price level of commercial vanilla cream dairy desserts samples.

Sample	Dairy ingredients [a]	Thickeners [a]	Colorants[a]	Price[b]
1	Semi-skimmed milk	Modified starch Carrageenan Xanthan gum	Tartrazine, cochineal	1.4
2	Milk Semi-skimmed milk	Modified starch Carrageenan Guar gum	Annatto	1
3	Milk Cream Semi-skimmed milk powder	Acetylated distarch adipate Gelatine	Tartrazine, cochineal	2.3
4	Milk Cream Dairy solids	Modified starch Carrageenan Fatty acid esters	Tartrazine, cochineal	2.5
5	Milk Cream	Modified starch Carrageenan Guar gum	Mixed carotenes	2.5
6	Milk Cream	Modified starch Carrageenan Guar gum	Mixed carotenes	1.7
7	Milk Cream Dairy solids	Modified starch Carrageenan Fatty acid esters	Tartrazine, cochineal	1.9

a. Declared in label.
b. Lower price considered as reference unit

2.2. Colour measurements

Colour was measured in a Hunter colorimeter, Labscan II model. Samples were contained in optical glass cells 3.8 cm high and 6 cm diameter. A 3.5 cm thick layer was covered with the white standard plate (X= 78.50; Y= 83.32; Z= 87.94) for measurement of diffused reflected light from the cell bottom using a 13 mm diaphragm aperture. Results were given in CIELAB system for illuminant D 65 and a 10º angle of vision. Registered parameters were: L^* (brightness), a^* (red component), b^* (yellow component), C^* (chroma), and h^* (hue). Two measurements were done on each sample.

2.3. Rheological measurements

Flow behaviour measurements were carried out in a Haake VT 550 viscometer, using concentric cylinders sensors (MV1 and MV3, with 1.05 and 1.38 radii ratios, respectively). Flow curves were obtained by recording shear stress values when shearing the samples at increasing shear rates from 1 to 200 s^{-1} in 60 s and down in reverse sequence in the same time (Tárrega et al, 2004). Data from the upward curve were fitted to the Herschel-Bulkley model (Eq. 1) using the Rheowin Pro Data software (version 2.93, Haake). In order to fit experimental data to this model a predetermined yield stress value is required (Holdsworth, 1993). In this case, yield stress (σ_0) value was previously obtained by fitting the experimental data to the Casson model (Eq. 2) and calculating the square of the ordinate intercept in the Casson plot. Apparent viscosity values at 10 s^{-1} (Eq.3) were calculated.

$$\sigma = \sigma_0 + K\dot{\gamma}^n \qquad (1)$$

$$\sigma^{0.5} = \sigma_0^{0.5} + K\dot{\gamma}^{0.5} \qquad (2)$$

$$\eta_{10} = (\sigma_0 + K \cdot 10^n) /10 \qquad (3)$$

Small amplitude oscillatory measurements were carried out in a controlled stress rheometer (RheoStress 1, Karslruhe, Germany), monitored by a Rheowin Projob Manager, using a serrated parallel plates sensor system (6 cm diameter and 1mm gap) to avoid wall slip phenomena. To determine the linear viscoelastic region stress sweeps were run at 1 Hz. Frequency sweeps were performed over the range f = 0.01-10 Hz and the values of storage modulus (G'), loss modulus (G''), loss angle tangent (tan δ) and complex viscosity (η*), as a function of frequency, were calculated using Rheowin Data Manager Software (Tárrega et al, 2005)

All measurements were run at 25±1ºC. The samples were allowed to rest 15 min after loading, before measurement. Two replicates were run and a fresh sample was loaded for each run.

2.4. Sensory evaluation

Sensory evaluation was made using ranking tests (ISO,1988a) by 42 assessors. They ranked the samples according to their colour (from light yellow to orange-yellow) and according to their thickness (from lower to higher thickness). Evaluation of colour sessions were carried out using a Colour Viewing Chamber equipped with illuminant D65. Light from this source was projected vertically on the sample and observed with an angle of 45º (ISO, 1999). Thickness evaluation was performed in a standardised test room (ISO 1988b) with normal white fluorescent illumination. Data acquisition was performed using Compusense Five v.3.6. (Compusense Inc., Guelph, Canada). The seven samples (30 ml), codified with three digits random numbers, were presented simultaneously. Mineral water was served to clean the mouth between samples.

2.5. Statistical analysis

One factor (sample) ANOVA was applied to the instrumental data. Principal Component Analysis (PCA) with varimax rotation was applied to the correlation matrix of the average values of colour parameters and to the correlation matrix of the rheological parameters average values. Both analyses were performed using the SPSS version 11.5 (SPSS Inc. Chicago, USA).

Friedman Analysis of Variance was applied to the sensory data obtained in the rank tests, significance of differences between samples were determined by the Fisher test (α=0.05), modified for non-parametric data (Meilgaard, Civille & Carr, 1999) using Compusense Five v.3.6. (Compusense Inc., Guelph, Canada). Correlations between sensory and instrumental data were determined using the Spearman correlation coefficient (ρ) (O' Mahony, 1986).

3. Results

3.1.Instrumental measurements

3.1.1. Colour

Reflectance spectra in the visible region (400-700 nm) for the seven dairy dessert samples are shown in Figure 1. For all of them the typical spectral curve for yellow-orange coloured materials, with maximum reflectance values at wavelengths over around 550 nm, can be observed. Significant differences (α=0.01) on brightness (L*), redness (a*), yellowness (b*), saturation (C*) and hue (h*) values for the seven samples were detected (Table 2). A wide range of redness values was found mainly due to the higher value of a* for sample 2. This sample showed a clear yellow-orange colour whereas the other samples, with negative a* values and b* values

ranging from 30.4 to 41.0, were perceived as yellow. Samples 5 and 6 were the lighter coloured (L*=86.7) and samples 1 and 2 were the darker ones (L*=76.6).

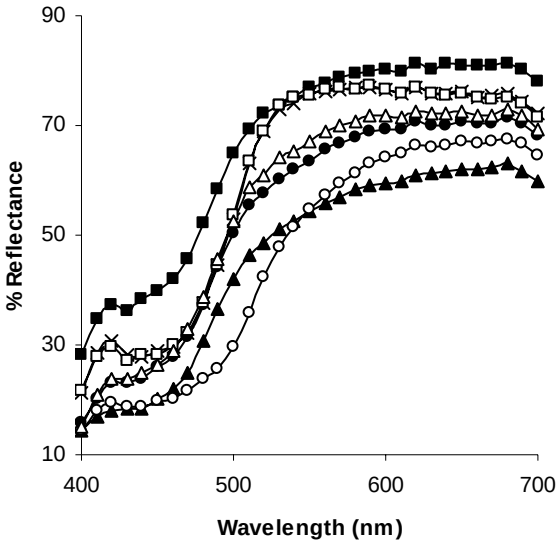

Figure 1. Spectral reflectance curves of vanilla dairy dessert samples: (▲) 1, (○) 2, (■) 3, (●) 4, (×) 5, (□) 6, (△) 7. Identification of samples in Table1.

Table 2. Average values of instrumental colour parameters for vanilla dairy dessert samples[1]. Identification of samples in Table 1.

Sample	L*	a*	b*	C*	h*
1	76.6^{a}	-1.0^{d}	38.2^{b}	38.2^{b}	91.5^{b}
2	76.6^{a}	6.8^{e}	41.0^{d}	41.6^{d}	80.6^{a}
3	88.5^{e}	-3.4^{b}	30.4^{a}	30.6^{a}	96.4^{e}
4	82.3^{b}	-2.0^{c}	37.7^{b}	37.8^{b}	93.1^{c}
5	86.7^{d}	-4.3^{a}	40.5^{cd}	40.7^{cd}	96.0^{e}
6	86.7^{d}	-4.7^{a}	41.0^{d}	41.2^{d}	96.5^{e}
7	83.6^{c}	-3.1^{b}	40.0^{d}	39.7^{c}	94.5^{d}

[1]Values within a column with different superscripts are significantly different (α= 0.05).

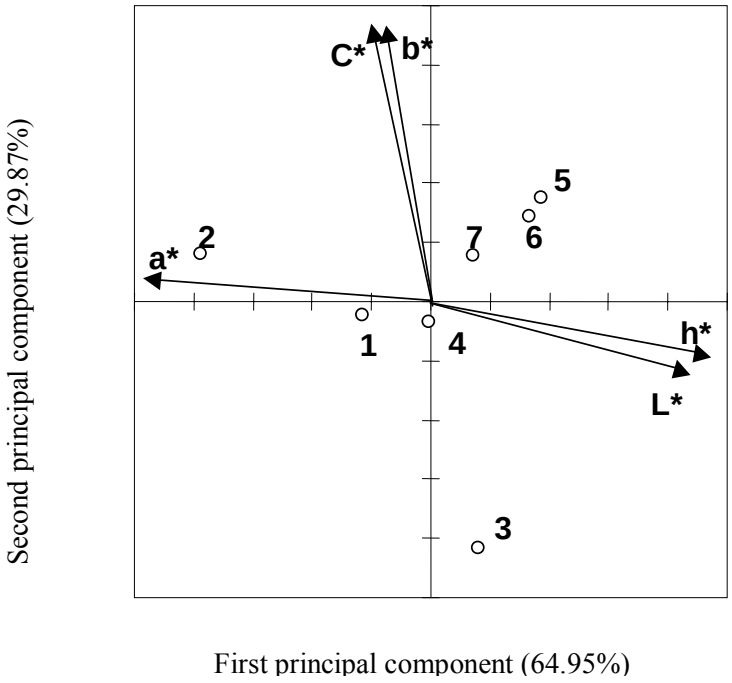

Figure 2. Principal component analysis plot for vanilla dairy desserts: instrumental colour parameters. Identification of samples in Table 1.

On applying PCA analysis to the average values of the instrumental colour parameters corresponding to the seven samples, the two first components showed eigen values higher than 1. The consideration of both components accounted for 94.82% of the total variability. The first component (PC1), explaining 64.95% of the variability, was strongly associated with L* (r=0.87), h* (r=0.97) and a* (r=-0.98) values. The second component (PC2) accounted for 29.87% of the variability and it was mainly associated with b* (r=0.99) and C* (r=0.98) values (Figure 2). PC1 clearly separated sample 2 on the left side, due to its high redness and lower brightness. Samples on the right side, mainly samples 5 and 6, were lighter. PC2 separated sample 3 on the lower part as the sample with less yellow intensity.

3.1.2. Rheology

As previously reported (Tárrega et al., 2004), all samples showed observable hysteresis loops when they were sheared during a complete cycle. On observing shear stress variation with shear rate all samples showed non-Newtonian shear-thinning flow with an apparent initial resistance to flow. This behaviour is in accordance with that observed by other authors in similar products (Mleko and Gustaw, 2002; Wischmann et al., 2002). In time dependent and non-Newtonian shear-thinning products, the perceived thickness is difficult to characterise because flow in the mouth is probably a combination of shear and elongational flow (van Vliet, 2002). However, some authors have found that oral thickness correlate with different flow parameters, depending on the flow behaviour of each particular product (Costell & Durán, 2000). In this work, experimental data of the upward curve for the seven natillas samples were fitted to Herschel and Bulkley model ($R^2 \geq 0.988$). The flow of samples was clearly pseudoplastic, showing flow indices (n) in the range between 0.45 and 0.59 (Table 3).The high yield stress values obtained (17.28 to 55.9 Pa) (Table 3) suggested that analysed samples have a real initial resistance to flow. Though these values were calculated by extrapolation- fitting experimental data to the Casson model- then being of an empirical rather than a rheological nature (Newis & Spaull, 1976) their practical use in the characterisation of this type of products has been recognized. The consistency index value (K) ranged from 2.18 $Pa.s^n$ for sample 2 to 5.11 $Pa.s^n$ for sample 7. Since K values depend on n values, the apparent viscosity at 10 s^{-1} values were used in the analysis of variance performed to study the differences in flow properties among samples. This value of the apparent viscosity was selected as a possible practical index of sensory viscosity according with the proposal of Shama and Sherman (1973). These authors suggested that the physical stimulus of sensory viscosity varies with flow characteristics, and for more viscous foods it

appears to be related with the shear stress, developed at an approximately constant shear rate ($\dot{\gamma}$ = 10 s^{-1}). Significant differences (α=0.05) in yield stress (σ_0), in flow index (n), and in apparent viscosity (η_{10}) values were detected between samples (Table 3). Samples 5 and 6 showed higher resistance to flow, more pseudoplastic flow and higher apparent viscosity value than the rest.

Table 3. Average values of flow behaviour parameters for vanilla dairy desserts[1]. Identification of samples in Table 1.

Sample	σ_0 (Pa)	n	η_{10}(Pa.s)
1	23.58^{b}	0.50^{b}	3.20^{b}
2	17.28^{a}	0.57^{d}	2.54^{a}
3	25.18^{b}	0.59^{e}	3.69^{c}
4	33.98^{c}	0.56^{d}	4.89^{d}
5	55.99^{e}	0.45^{a}	6.74^{e}
6	55.42^{e}	0.46^{a}	6.68^{e}
7	50.03^{d}	0.53^{c}	6.73^{e}

[1] Values within a column with different letter superscripts are significantly different (α= 0.05).

All samples showed mechanical spectra typical of a weak gel with G' values higher than G'' (Tárrega et al., 2005). For semisolid products with viscoelastic behaviour several authors have obtained a good correlation between oral thickness and small deformation measurements at an oscillatory frequency of 50 rad s^{-1} (Richardson, Morris, Ross-Murphy, Taylor & Dea, 1989 ; Hill, Mitchell & Sherman, 1995). Values of G', G'', tan δ and η∗ values at a frequency of 1 Hz and η∗ values at 7.95 Hz (equivalent to 50 rad.s^{-1}) were determined. (Table 4). One factor ANOVA showed significant differences (α=0.05) between samples for all parameters (Table 4).

Table 4. Average values of G', G'', tan δ and η* for vanilla dairy dessert samples[1]. Identification of samples in Table 1.

Sample	G' (Pa) [2]	G'' (Pa) [2]	tan δ [2]	η* (Pa.s) [2]	η^*_{50} (Pa.s) [3]
1	3.0^{a}	2.5^{a}	0.844^{d}	0.62^{a}	0.19^{a}
2	19.9^{b}	5.1^{b}	0.255^{b}	3.26^{b}	0.61^{b}
3	35.4^{c}	7.9^{c}	0.224^{a}	5.77^{c}	0.92^{c}
4	35.8^{c}	11.7^{d}	0.328^{c}	6.00^{c}	1.11^{cd}
5	51.3^{d}	11.1^{d}	0.218^{ab}	8.34^{d}	1.33^{d}
6	52.6^{d}	11.8^{d}	0.228^{a}	8.59^{d}	1.39^{d}
7	31.0^{bc}	10.7^{d}	0.344^{c}	5.23^{c}	1.01^{c}

[1] Values within a column with different superscripts are significantly different (α= 0.05).
[2] Values determined at frequency = 1 Hz.
[3] Values determined at frequency =7.95 Hz (50 rad.s^{-1})

PCA analysis of average values of both large and small-scale deformation rheological parameters showed that the first component accounted for 71.12% of data variability and up to 89.99% was explained by the first two components. The first component was strongly associated with viscoelastic parameters: G' (R^2= 0.87), G'' (R^2= 0.82), tan δ (R^2=-0.96) and η∗ (R^2= 0.87) and the second component was associated with flow parameters: σ_0 (R^2= 0.88), K (R^2= 0.71), n (R^2= -0.88) and η_{10} (R^2= 0.86) (Figure 3). Component 1 separated clearly sample 1, with lower G' and G'' values and with the higher value of tan δ (0.84). This value indicate a higher contribution of viscous component on its viscoelastic behaviour. The rest of samples showed the typical behaviour of gelled systems, with higher values for the two moduli and tan δ values that ranged from 0.22 to 0.34 (Table 4). The second component separated a group of three samples (5, 6 and 7), located in the upper half, with higher flow plasticity ($50.03 < \sigma_0 < 55.99$ Pa) and higher viscosity ($6.68 < \eta_{10} < 6.73$ Pas), from sample 2, located in the lower half, which showed the lower yield stress value (17.28 Pa) and the lower viscosity (2.54 Pas).

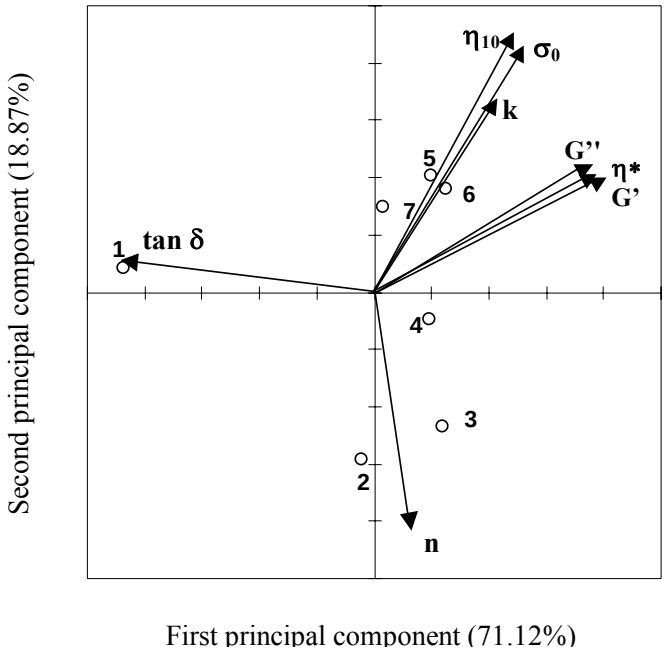

Figure 3. Principal component analysis plot for vanilla dairy desserts: rheological parameters. Identification of samples in Table 1.

3.2. *Sensory analysis*

Analysis of results obtained from the ranking tests showed significant differences (α=0.05) in samples colour. Friedman F value was 249.63 (theoretical F value being 12.59 for α=0.05). Sample 3 was ranked as with less intensity yellow colour and sample 2 was ranked as with more yellow-orange colour than the rest of samples (α=0.05) (Figure 4). Although these perceived differences were in agreement with the samples position in the map obtained by Principal Component Analysis of instrumental colour parameters (Figure 2), samples 5 and 6, with similar position in the latter map, were perceived as significantly different in colour. The same observation can be made about samples 1 and 4.

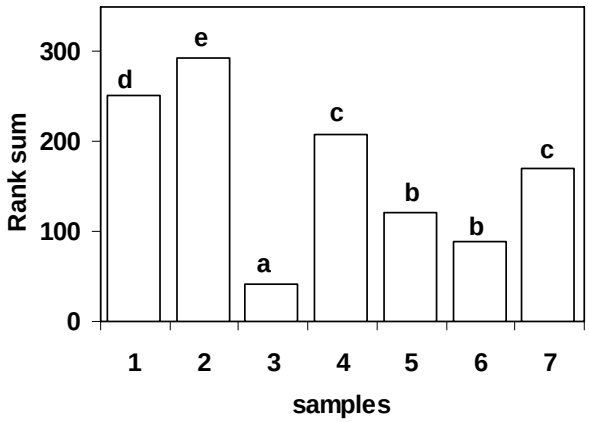

Figure 4. Sensory evaluation of colour for vanilla dairy desserts. Different letters on top of bars mean significant differences (α=0.05). Identification of samples in Table 1.

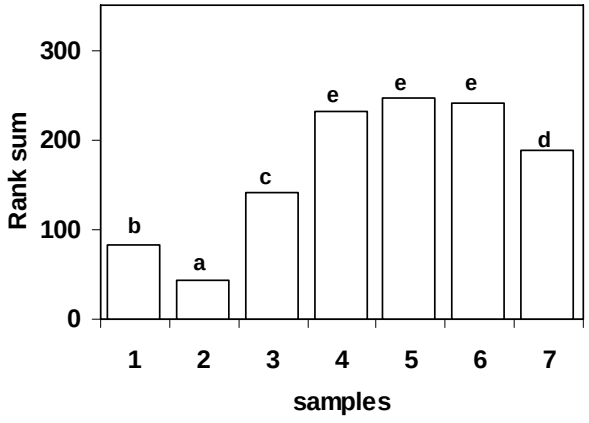

Figura 5 Sensory evaluation of consistency for vanilla dairy desserts. Different letters on top of bars mean significant differences (α=0.05). Identification of samples in Table 1

On ranking thickness of samples, significant differences were also found ($F_{Friedman}$=199.98 , $F_{theoretical}$ =12.59, α=0.05). Sample 2 was perceived as the sample with the lowest consistency and no significant differences were found between samples 4, 5 and 6, which were perceived as thicker than the rest (Figure 5).

3.3. *Relationship between instrumental and sensory data*

As reported above, significant differences in colour and in texture of commercial dairy dessert samples were detected both by instrumental and by sensory methods. To explore the relationships between them, Spearman Analysis was used to establish correlations between the colour perceived and the instrumental colour parameters as well as those between the oral thickness and the rheological parameters.

The results showed a significant positive correlation between sensory colour and parameter a* (ρ=0.89), and significant negative correlations with parameters L* and h* (ρ=-0.96 for both parameters). No significant correlations were found between sensory colour data and b* and C* parameters (ρ=0.32 for both parameters).

Oral thickness of the dairy desserts showed a good correlation with the yield stress values (ρ=0.96) and with the apparent viscosity values at 10 s^{-1} (ρ=0.89). These results are in agreement with the comments of van Vliet (2002) about that the assessment of thickness for products with a high viscosity or a yield stress can be related with the pressure (stress) required to produce significant flow, and with the proposal of Shama & Sherman (1973) about that viscosity under steady shear at 10 s^{-1} had a good correlation with perceived thickness for semisolid products. From viscoelastic parameters the storage modulus at 1 Hz and the complex viscosity at 7.95 Hz (50 rad s^{-1}) showed higher correlation coefficients (0.92 for both parameters) than the loss modulus (ρ= 0.86) and the complex viscosity at 1Hz (ρ=0.89). Good correlation between the complex viscosity at 50 rad s^{-1} and perceived thickness was shown by Richardson et al. (1989) in true solutions and in weak gels, and by Hill et al. (1995) in lemon pie fillings. For practical purposes it can be concluded that the initial resistance to flow (yield stress

value) and the complex viscosity at 50 rad s^{-1} can be useful indices of oral thickness for semisolid dairy desserts.

Acknowledgements

To MEC (formerly MCyT) of Spain for financial support (Project AGL 2003-0052) and for the fellowship awarded to author Tárrega. To Dr. Luis Durán for his valuable contribution.

References

Batista, P., Nunes, M. C. & Sousa, I. (2002). Physical characterisation of commercial dairy desserts. In F.J. Martínez Boza, A. Guerrero, P. Partal, J.M. Franco & J. Muñoz., *Progress in Rheology Theory and Applications.* Publicaciones Digitales S.A. Sevilla, Spain, 449-452.

Conde-Petit, B., Nuessli, J., Handschin, S. & Escher, F. (1998). Comparative characterisation of aqueous starch dispersions by light microscopy, rheometry and iodine binding behaviour. *Starch-Starke*, 50,184-192.

Costell, E & Durán L (2000). Sensory and instrumental measures of viscosity. In J E Lozano, C. Añón, E. Parada-Arias & G V Barbosa-Cánovas (eds), *Trends in Food Engineering*. Technomic Publ. Co. Inc., Lancaster, USA, 53-64.

De Vries, J. (2002). Interaction of carrageenan with other ingredients in dairy dessert gels. In P.A. Williams and G.O. Philips, *Gums and stabilisers for the food industry 11*. Royal Society of Chemistry, Cambridge, UK, 201-210.

De Wijk, R. A., Rasing, F. & Wilkinson, C. L. (2003). Texture of semi-solids: Sensory flavor-texture interactions for custard desserts. *Journal Of Texture Studies*, 34, 131-146.

De Wijk, R. A., van Gemert, L. J., Terpstra, M. E. J., & Wilkinson, C. L.(2003). Texture of semi-solids; sensory and instrumental measuraments on vanilla custard desserts. *Food Quality and Preference*, 14, 305-307.

Depypere, F., Verbeken, D., Thas, O. & Dewettinck, K. (2003). Mixture design approach on the dynamic rheological and uniaxial compression behaviour of milk desserts. *Food Hydrocolloids*, 17, 311-320.

Hill, M.A., Mitchell, J.R. and Sherman, P.A. (1995). The relationship between the rheological and sensory properties of a lemon pie filling. *Journal of Texture Studies* 26, 457-470.

Holdsworth, S. D. (1993). Rheological models used for the prediction of the flow properties of food products. *Transactions of the Institution of Chemical Engineers*, 71, 139-179.

ISO (1988a). Sensory analysis. Methodology. Ranking. Standard no. 8587. Geneva, Switzerland.

ISO (1988b). Sensory analysis. General guidance for design of test rooms. Standard no. 8589. Geneva, Switzerland.

ISO (1999). Sensory analysis. General guidance and test method for assessment of the colour of foods. Standard 11037. Geneva, Switzerland.

Lethuaut, L., Brossard, C., Rousseau, F., Bousseau, B. & Genot. C. (2003). Sweetness-texture interactions in model dairy desserts: effect of

sucrose concentration and the carrageenan type. *International Dairy Journal*, 13, 631-641.

Meilgaard, M., Civille, G.V. & Carr, B.T. (1999). *SensoryEvaluation Techniques*, 3rd ed. CRCPress, Inc., Boca Raton (FL), USA

O'Mahony, M. (1986). *Sensory Evaluation of Food: Statistical Methods and Procedures*. Marcel Dekker, New York (NY), USA.

Parker, A. & Tilly, G. (1994). Thixotropic carrageenan gels and dairy desserts. In G.O. Philips., P.A. Williams and D.J. Wedlock, *Gums and stabilisers for the food industry 7*. IRL Press, Oxford, UK, 393-401.

Richardson, R.K., Morris, E.R., Ross-Murphy, S.B., Taylor, L.J. & Dea, I.C.M. (1989). Characterization of the perceived texture of thickened systems by dynamic viscosity mea-surements. *Food Hydrocolloids*, 3, 175-191.

Shama, F. & Sherman, P. (1973). Identification of stimuli controlling the sensory evaluation of viscosity II. Oral methods. *Journal of Texture Studies*, 4, 11-118.

Tárrega, A., Durán, L. & Costell E. (2004). Flow behaviour of semisolid dairy desserts. Effect of temperature. *International Dairy Journal* 14, 345-353.

Tárrega, A., Durán, L. & Costell E. (2005). Rheological characterization of semisolid dairy desserts. Effect of temperature. *Food Hydrocolloids* 19, 133-139.

Van Vliet, T. (2002). On the relation between texture perception and fundamental mechanical parameters for liquids and time dependent solids. *Food Quality and Preference*, 13, 227-236

Verbeken, D., Thas, O. & Dewettinck, K. (2004). Textural properties of gelled dairy desserts containing kappa-carrageenan and starch. *Food Hydrocolloids*,18, 817-823.

Wischmann, B., Norsker, M. & Adler-Nissen, J. (2002). Food product models developed to evaluate starch as food ingredient. *Nahrung/ Food*, 46, 167-173.

VANE YIELD STRESS OF NATIVE AND CROSS-LINKED STARCH DISPERSIONS IN SKIM MILK: EFFECT OF STARCH CONCENTRATION AND λ-CARRAGEENAN ADDITION.

A. Tárrega[1*], E. Costell[1] and M.A. Rao[2]

[1]*Instituto de Agroquímica y Tecnología de Alimentos (CSIC). P.O. Box 73, 46100 Burjassot, Spain.*

[2]*Department of Food Science and Technology, Cornell University, Geneva, NY 14456-0462, USA*

Abstract

The effects of starch concentration and λ-carrageenan addition on the yield stress values of native and cross-linked waxy maize starch-milk systems were studied. Static yield stress ($\sigma_{0\text{-}S}$) and dynamic yield stress ($\sigma_{0\text{-}D}$) of each dispersion were measured using the vane method before and after breaking down its structure by shearing, respectively. Increases in values of $\sigma_{0\text{-}S}$ with concentration of starch and λ-carrageenan were higher for cross-linked starch than those of native starch. Dynamic yield stress values of cross-linked starch also increased with concentration of starch and λ-carrageenan. In contrast, for native starch samples, dynamic yield stress values were very low and did not vary much with concentration of either starch or λ-carrageenan indicating that the structures responsible of the yield stresses were highly sensitive to shearing.

Key Words: Yield stress, Vane method, Starch, Milk, λ-carrageenan.

*Corresponding author. Tel.:+34-96-3900022; Fax: +34-96-3636301.
E-mail address: atarrega@iata.csic.es

1. Introduction

The rheological behaviour of commercial dairy desserts (Batista et al. 2002, Tárrega et al. 2004 and 2005a) or of their corresponding model systems (Wischman et al. 2002, Depypere et al 2003 and Vélez-Ruiz et al. 2005), in general, showed time dependent, shear-thinning flow behaviour, with a measurable initial resistance to flow, as well as viscoelastic properties typical of structured gels. That behaviour was strongly influenced by the particular characteristics of their ingredients, including: milk fat content, type and concentration of starch and hydrocolloid, and their crossed interactions. An important aspect of this behaviour is the initial resistance to flow of these products. Oral thickness of the commercial dairy desserts showed a good correlation with the yield stress values (Tárrega, unpublished data) and this result is in agreement with the comments of van Vliet (2002) about that the assessment of thickness of products with a high viscosity or with a yield stress can be related with the pressure (stress) required to produce a significant flow.

Although the concept of yield stress as a true material property has been questioned (Barnes and Walters, 1985), its practical usefulness in process design and modelling, and in quality control of foods is generally accepted (Nguyen and Boger, 1992). The existence of a yield stress in a material's flow indicates that there is a cross-linked or other interactive structure which must be broken down before flow can occur at an appreciable rate. Thus, the yield stress of a food can be considered to be the minimum stress required to initiate flow, and that it is a measure of the strength of the material's network. There are several ways to evaluate the yield stress of foods. Indirect methods involve the extrapolation of the shear stress-shear rate data to zero shear rate, with or without the help of a flow model such as Bingham, Casson or Herschel-Bulkley (Canet et al, 2005). Although the yield stress values thus obtained are dependent on the model used to fit the data and on

the range of shear rates applied, they are relatively easy to determine; yield stress values of starch dispersions heated in water or milk were obtained by applying the Herschel-Bulkley and Casson models (Acquarone and Rao 2003, Nayouf et al, 2003, Vélez-Ruiz et al, 2005, Tárrega et al, 2005b).

One direct and simple method to measure yield stress of structured products is by vane rheometry. The particular advantages of the vane geometry are its simplicity of fabrication, ease of cleaning and more than anything else, minimal destruction of the sample structure during loading and its elimination of wall-slip effects (Barnes and Nguyen, 2001). Vane rheometry has been used to measure directly the yield stress of different foods (Qiu and Rao 1988; Briggs et al. 1996; Rao and Steffe 1997; Truong et al. 2003), as well as that of aqueous starch dispersions. Genovese and Rao (2003) studied the structural differences in cross-linked, tapioca and Amioca starch dispersions, by measuring yield stress before (static yield stress) and after breaking down its structure (dynamic yield stress) with the vane method. Based on earlier studies on dispersions (Michaels and Bolger, 1962; Metz et al. 1979), they suggested that the static yield stress is due to contributions of bonding, network, and viscous components. More recently, Genovese et al. (2004) studied the effect of sucrose or fructose on the yield stress of gelatinised Amioca starch dispersions using both the vane method and the indirect method by extrapolation of shear stress-shear rate data fitted to Herschel-Bulkley model.

Starch is frequently used in combination with carrageenan in the formulation of dairy products. When starch is heated in water, starch granules swell and after cooling a viscous paste is formed, a biphasic structure composed of swollen starch granules in a continuous phase. In native starch, the continuous phase is essentially an aqueous solution of the amylose leached during granule swelling (Nguyen et al. 1998, Thebaudin et al. 1998). Native and modified starches show different behaviours during heating and cooling

processes. Modified starch shows higher thermomechanical resistance and if the granules remain whole after pasting, the resultant system is an aqueous dispersion whose rheological behaviour mainly depends on the granules' volumetric fraction and on their rigidity or deformability (Tattiyakul and Rao, 2000; Nayouf et al. 2003).

Quantitative changes in the rheological response of these systems may be originated by substituting milk for water (Matser and Steeneken, 1997; Tárrega et al. 2005b) or by adding different types of hydrocolloids (Umadevi and Raghavendra, 1987; Alloncle and Doublier, 1991, Liu and Eskin, 1998). For commercial dairy products, carrageenans, mainly κ- and ι-carrageenan, are considered to be the most suitable hydrocolloids due to their capability of combining into double helices and to their interactions with casein, with which they form network structures. Lambda-carrageenan molecules have a strongly anionic charge, due to the presence of three sulphate groups, and they do not form gels in aqueous solutions, causing only an increase in viscosity. However it has been shown that λ-carrageenan is able to form gels in the presence of milk (Langendorff et al, 2000; Shchipunov and Chesnokov, 2003). According to the former authors, although λ-carrageenan is not capable of combining into double helices, it shows attractive interactions with casein micelles, that can induce binding of the micelles and the formation of a carrageenan/casein network on cooling.

The objectives of this work were to study the effects of starch and of λ-carrageenan concentrations on the vane yield stress values of both native and cross-linked waxy maize starch-skim milk dispersions.

2. Materials and methods

2.1. Materials

Two types of waxy maize starch: cross-linked starch (Purity®-W), native starch (Amioca) from National Starch and Chemical Co, NJ, USA and λ-carrageenan (Satiagum^{TM} ADC 25) from Degussa Texturant Systems, NE, USA were used in this study. Skim milk was prepared by dissolving 12% (w/w) commercial skim milk powder in distilled water 24 h in advance.

2.2. Sample preparation

To study of the effect of starch concentration, a first lot of samples, containing a fixed amount of skim milk (80%) and varying in starch concentration (4.0, 4.5, 5.0 and 5.5 %), and in the type of starch (native and cross-linked starch) were prepared. To study the effect of λ-carrageenan addition, a second lot of samples, containing fixed amounts of each type of starch (4.0%) and skim milk (80%) were prepared varying the λ-carrageenan concentration (0, 0.02, 0.03, 0.04, 0.05 and 0.06%). Samples (500g) were prepared as follows: a concentrated suspension of starch in water was heated to 50ºC, which was below the gelatinisation temperature. The starch suspension was added to the hot (87 ºC) milk-carrageenan mixture, under magnetic stirring, until the final mixture temperature was 80ºC. The sample was held at this temperature for 10 min by heating in a rotating round-bottom flask submerged in a thermostatic bath (Rotavapor, Büchi, Switzerland). Finally the sample was cooled in a water-ice bath until it reached a temperature of about 20ºC.

2.3. Rheological measurements

Samples were placed into a jacketed stainless-steel vessel (D=7.2 cm, H=11.7 cm) connected to a constant temperature circulator (Haake DC30-k20, Paramus, N. J., USA) and were allowed to equilibrate for 2 h to recover their structure and reach the measurement temperature: 5 ± 1ºC. Rheological measurements were carried out using a Haake Rotovisco RV30 viscometer equipped with a 6-blade vane impeller (D=4cm, H= 6cm) and monitored by a Haake Rotation v. 3.0 software. The static yield stress ($\sigma_{0\text{-}S}$) of the undisrupted sample was measured by recording the magnitude of torque with the vane rotating at a constant speed of 0.05 rpm. Recorded torque values were converted to vane stress values using the following equations:

$$\sigma = T/K \qquad (1)$$

$$K = \frac{\pi D^3}{2}\left(\frac{H}{D} + \frac{1}{3}\right) \qquad (2)$$

where σ (Pa) is the vane stress, T is the torque and K is the vane parameter that depends on the diameter (D) and height (H) of the vane impeller. After disrupting the sample structure by shearing it from 1 to 258.6 rpm in 10 min up and down in 10 min, the yield stress was measured again. This value was considered to be the dynamic yield stress ($\sigma_{0\text{-}D}$) of the disrupted sample. Each measurement was done in duplicate.

2.4. Statistical analysis

ANOVA, including two factors with interactions, was used to study the combined effect of starch type and starch concentration on static ($\sigma_{0\text{-}S}$) and on dynamic ($\sigma_{0\text{-}D}$) yield stress values of starch-milk dispersions and to study

the combined effect of starch type and carrageenan concentration on $\sigma_{0\text{-}S}$ and $\sigma_{0\text{-}D}$ values of starch-milk- λ-carrageenan dispersions. The Fisher test (α=0.05) was used to calculate the minimum significant difference. All calculations were carried out with the Statgraphics Plus 4.1 software.

3. Results

3.1. Shear stress-time curves

The shear stress-time curves for undisrupted and disrupted samples were registered and some of them are represented as an example in figure 1. The curves showed an initial increase in stress, that represents the elastic response of the material, followed by a decrease of the stress values, associated with the gradual structure breakdown (Truong et al. 2003). Stress decay in the disrupted samples was very small, due to the rupture of the structural bonds during shearing (Genovese and Rao, 2003). Static yield stress ($\sigma_{0\text{-}S}$) and dynamic yield stress ($\sigma_{0\text{-}D}$) values were obtained from the peak of the curves corresponding to the undisrupted and to the disrupted samples, respectively, and the angular deformation of the sample at this point (θ_F) was calculated using the following equation:

$$\theta_F = \frac{2\pi}{60} N.t \qquad (3)$$

where t (s) is the time required to reach the maximum stress and N correspond to the rotational speed (rpm).

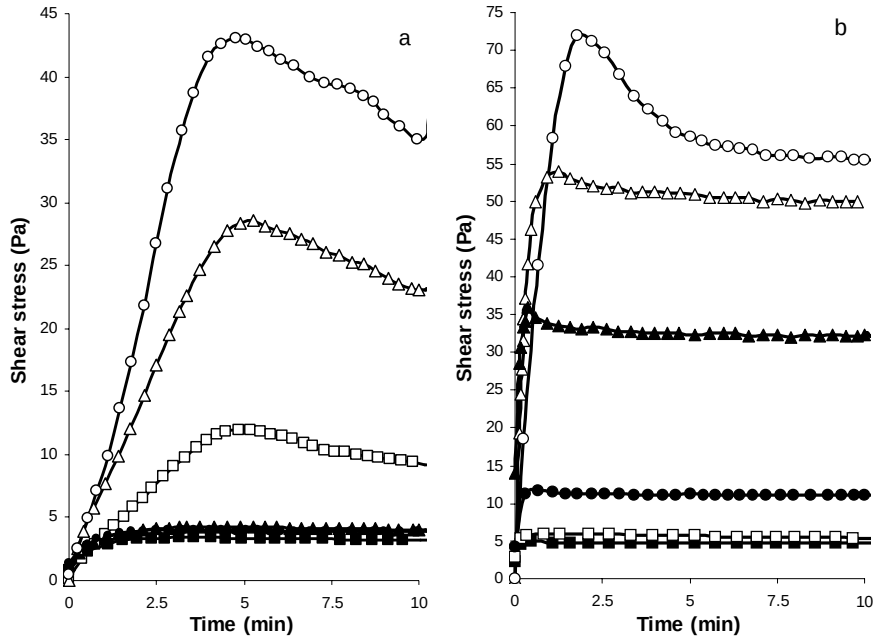

Figure 1. Vane stress versus time curves obtained at 0.05 rpm for native (a) and cross-linked (b) starch samples with different compositions: 4% starch (■), 5% starch (▲) and 4% starch +0.03% λ-carrageenan (●). Undisrupted sample (empty symbols) and disrupted samples (filled symbols).

Table 1. Values of angular deformation at failure (θ_F) for undisrupted and disrupted starch samples for different starch types and concentrations.

		Undisrupted sample	Disrupted sample
Starch type	**Starch concentration (%)**	**θ_F (rad)**	**θ_F (rad)**
Cross-linked	**4.0**	0.41	0.12
	4.5	0.41	0.11
	5.0	0.41	0.15
	5.5	0.40	0.18
Native	**4.0**	1.63	0.99
	4.5	1.74	0.90
	5.0	2.07	0.87
	5.5	1.80	0.99

Table 2. Values of angular deformation at failure (θ_F) for undisrupted and disrupted 4% starch samples for different starch types and λ-carrageenan concentrations.

		Undisrupted sample	Disrupted sample
Starch type	**λ-carrageenan concentration (%)**	**θ (rad)**	**θ (rad)**
Cross-linked	**0**	0.41	0.12
	0.02	0.58	0.11
	0.03	0.57	0.15
	0.04	0.69	0.18
	0.05	0.66	0.18
	0.06	0.65	0.18
Native	**0**	1.63	0.99
	0.02	1.66	0.92
	0.03	1.55	0.78
	0.04	1.64	1.09
	0.05	1.63	1.02
	0.06	1.44	0.92

The values of angular deformation at failure mainly depended on the type of starch, being higher in the case of native starch-milk dispersions than in cross-linked starch milk-dispersions, indicating that the latter reached the failure point at lower angular deformations and showed a more "brittle" behaviour (Table 1). This observation is in agreement with the data obtained by Genovese and Rao (2003) in aqueous dispersions of cross-linked waxy maize, tapioca and Amioca starches. They observed that cross-linked waxy maize starch dispersion yielded at lower angular deformation than tapioca and Amioca starch dispersions. The values of deformation at failure were not significantly affected by the starch concentration (Table 1) or by the addition of λ-carrageenan (Table 2).

3.2. Effect of starch concentration on $\sigma_{0\text{-}S}$ and $\sigma_{0\text{-}D}$ values

The effects of starch concentration and of type of starch, on static ($\sigma_{0\text{-}S}$) and dynamic yield stress ($\sigma_{0\text{-}D}$) values were studied in the starch-milk

dispersions. For both parameters, the effect of the interaction, starch type-starch concentration was significant (F_{int} = 47.41, p< 0.001, for $\sigma_{0\text{-}S}$ and F_{int} = 34.94, p<0.001, for $\sigma_{0\text{-}D}$), which means that the effect of starch concentration on both parameters was different depending on the starch type. The static yield stress values increased with starch concentration for both native and cross-linked starch dispersions (Figure 2).

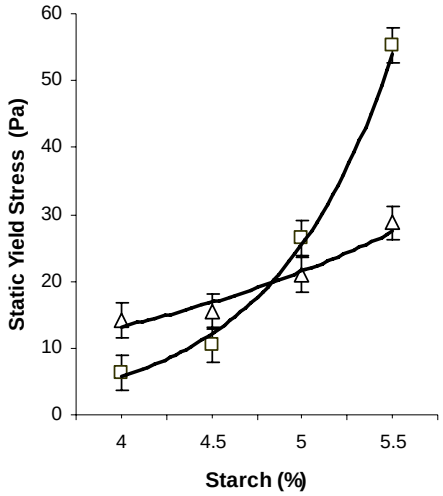

Figure 2. Variation of static yield stress values with starch concentration for cross-linked (□) and native (△)starch samples and the corresponding fits to exponential equations (—).

The increments were higher for cross-linked starch dispersions, which at 4 and 4.5 % starch concentration showed lower $\sigma_{0\text{-}S}$ values than native starch dispersions, while at 5 and 5.5% starch concentration they were higher. The variation of $\sigma_{0\text{-}S}$ stress values with starch concentration for native and cross-linked starch followed an exponential function (eq. 4 and eq.5, respectively).

$$\sigma_{0-S} = 2.7 \cdot e^{0.75 \cdot [\%Starch]} \qquad R^2 = 0.991 \qquad (4)$$

$$\sigma_{0-S} = 10.3 \cdot e^{0.24 \cdot [\%Starch]} \qquad R^2 = 0.951 \qquad (5)$$

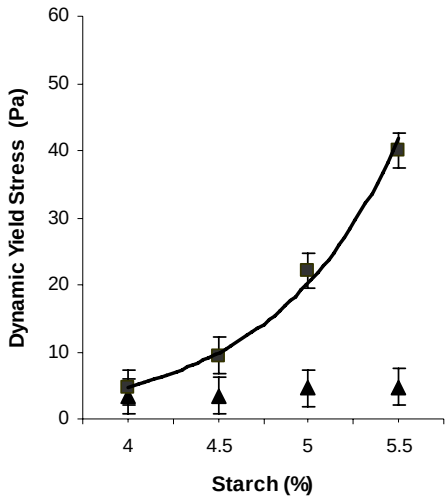

Figure 3. Variation of dynamic yield stress values with starch concentration for cross-linked (■) and native (▲) starch samples; line (—) indicates fit to exponential equation for cross-linked starch.

As expected, the values of yield stress after shearing ($\sigma_{0\text{-}D}$) (Figure 3) were lower than $\sigma_{0\text{-}S}$ values. The $\sigma_{0\text{-}D}$ values for native starch samples were very low and they did not vary with starch concentration, indicating that in these dispersions the structure responsible for the yield stress was highly sensitive to shearing and that most of the structural bonds were broken. For cross-linked starch, the variation of $\sigma_{0\text{-}D}$ values with starch concentration followed the same trend as that of $\sigma_{0\text{-}S}$ values, i.e., they increased following an exponential function (eq. 6).

$$\sigma_{0-D} = 2.32 \cdot e^{0.73\cdot[\%\text{Starch}]} \qquad R^2 = 0.9961 \qquad (6)$$

According to Genovese and Rao (2003), when yield stress is calculated from vane mixer data, the static yield stress ($\sigma_{0\text{-}S}$) can be considered to be the total failure stress of the undisturbed starch dispersion and the magnitude of the difference between $\sigma_{0\text{-}S}$ and $\sigma_{0\text{-}D}$ could be associated with the stress required

to break the bonds, $\sigma_{0\text{-}B}$, that contributed to the initial resistance to flow of the material. The ratio of this difference to the total yield stress, $(\sigma_{0\text{-}B}/\sigma_{0\text{-}S})$, in the studied starch dispersions represents the relative contribution of the stress required to break the bonding to the total stress necessary to initiate flow (Figure 4). The contribution of bonding was higher in the native starch dispersions (70-80%) than in the cross-linked ones (10-20%), probably due to the role of leached amylose in the former in the formation of bonds.

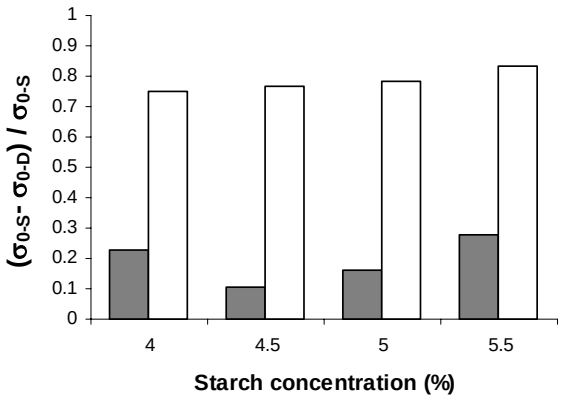

Figure 4. Effect of starch concentration on the contribution of stress required to break the bonding ($\sigma_{0\text{-}S}$-$\sigma_{0\text{-}D}$) relative to the total stress necessary to initiate flow ($\sigma_{0\text{-}S}$) for cross-linked (■) and native (□) starch dispersions

3.3. Effect of λ-carrageenan concentration on $\sigma_{0\text{-}S}$ and $\sigma_{0\text{-}D}$ values

For both $\sigma_{0\text{-}S}$ and $\sigma_{0\text{-}D}$values, ANOVA results showed a significant interaction between λ-carrageenan concentration and starch type (F_{int} = 26.43, $p<0.001$ for $\sigma_{0\text{-}S}$ and F_{int} = 17.01, $p<0.001$ for $\sigma_{0\text{-}D}$). The $\sigma_{0\text{-}S}$ values increased with λ-carrageenan concentration but the magnitude of the increase depended on the type of starch. Cross-linked starch samples, which contained intact granules, showed a higher increase of $\sigma_{0\text{-}S}$ with λ-carrageenan concentration than native starch dispersions (Figure 5).

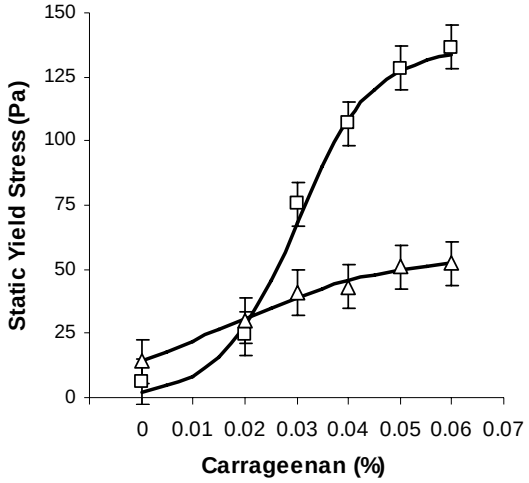

Figure 5. Variation of static yield stress values with λ-carrageenan concentration for 4% cross-linked (□) and 4% native (△) starch dispersions, and the corresponding fits to sigmoid equations (—).

The variation of $\sigma_{0\text{-}S}$ with λ-carrageenan concentration followed a sigmoid function (eq. 7 for native starch and eq. 8 for cross-linked starch) indicating that the $\sigma_{0\text{-}S}$ values increased with the addition of λ-carrageenan up to a limit.

$$\sigma_{0-S} = \frac{55.71}{1+10^{\frac{0.0168-[\%\text{Carrageenan}]}{0.036}}} \qquad R^2 = 0.990 \qquad (7)$$

$$\sigma_{0-S} = \frac{136}{1+10^{\frac{0.03-[\%\text{Carrageenan}]}{0.017}}} \qquad R^2 = 0.992 \qquad (8)$$

This behaviour can be explained by the ability of λ-carrageenan to bridging casein micelles. According to the observations of Shchipunov and Chesnokov (2003) the model, according to which the network structure composes of polysaccharide molecules and casein micelles acting as its

nodes, rather well explains the effect of carrageenan in milk systems. For κ- and ι-carrageenan, the stabilisation of the gel network is achieved by crosslinking of chain fragments between the micelles by double helices. For λ-carrageenan, gelling is ensured only by binding with casein micelles. As the amount of λ-carrageenan increase, the casein molecules get saturated and no further association with λ-carrageenan molecules can occur, that would increase the gel network strength and consequently the $\sigma_{0\text{-}S}$ values. On the other hand, the fact that the effect of λ-carrageenan concentration on $\sigma_{0\text{-}S}$ values showed a similar trend for both native and crosslinked starch may indicate that the increase in $\sigma_{0\text{-}S}$ with λ-carrageenan concentration could be attributed in part to the increase in the effective starch concentration, due to the ability of λ-carrageenan for binding water.

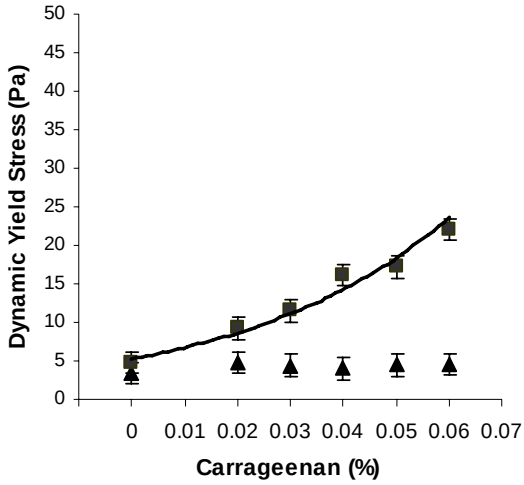

Figure 6. Variation of dynamic yield stress values with λ-carrageenan concentration for 4% cross-linked (■) and 4% native (▲) starch dispersions in milk; line (—) indicates fit to exponential equation for cross-linked starch.

The effect of λ-carrageenan addition on $\sigma_{0\text{-}D}$ values was smaller than that on $\sigma_{0\text{-}S}$ values and only in the case of cross-linked starch samples $\sigma_{0\text{-}D}$ values

increased significantly with λ-carrageenan concentration (Figure 6), following an exponential function (eq. 9)

$$\sigma_{0-D} = 5.22 \cdot e^{25.1 \cdot [\%\text{Carrageenan}]} \qquad R^2 = 0.974 \qquad (9)$$

That the presence of λ-carrageenan may have increased the effective concentration of the intact cross-linked starch granules could explain the increase in $\sigma_{0\text{-}D}$ values with increase in λ-carrageenan concentration.

The ratio of $\sigma_{0\text{-}B}$ ($\sigma_{0\text{-}B}=\sigma_{0\text{-}S}-\sigma_{0\text{-}D}$) to the total yield stress ($\sigma_{0\text{-}S}$) for dispersions with different λ-carrageenan concentration (Figure 7) indicated that the contribution of bonding increased due to the presence of λ-carrageenan-casein network for both native and cross-linked starch dispersions. For the cross-linked starch dispersions, compared to the control sample (0% carrageenan), the relative increase in bonding was high at 0.02% λ-carrageenan concentration and it did not change much over the concentration range 0.03 to 0.05%. Further, comparison with Figure 4 shows that λ-carrageenan-casein network played a major role in the contribution of bonding of the cross-linked starch dispersions.

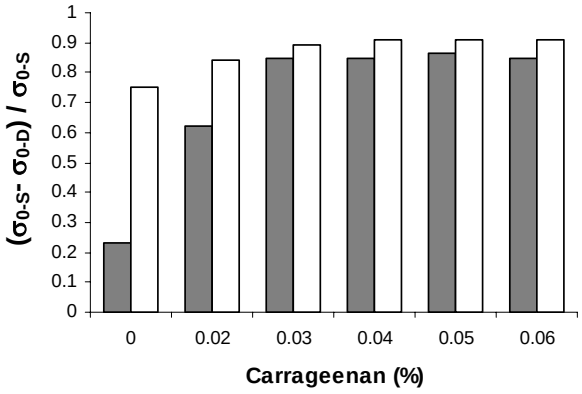

Figure 7. Effect of λ-carrageenan concentration on the contribution of stress required to break the bonding ($\sigma_{0\text{-}S}-\sigma_{0\text{-}D}$) relative to the total stress necessary to initiate flow ($\sigma_{0\text{-}S}$) for 4% cross-linked (■) and 4% native (□) starch dispersion.

3.4. Texture map

Traditionally the textural characterisation of viscoelastic food has ben carried out using compression or torsion tests. Truong et al. (2002) observed that the grouping of samples in the texture map generated from compresion test was similar to that generated from vane test. A plot of vane yield stress (failure stress) against angular deformation (or strain) can provide us a "texture map" of the samples and it has been used to describe some textural differences between dispersions of different starch types (Genovese and Rao, 2003). The plot obtained in this study (Figure 8) indicated that samples containig amioca starch showed more "rubbery" characteristics than samples containing cross-linked starch.

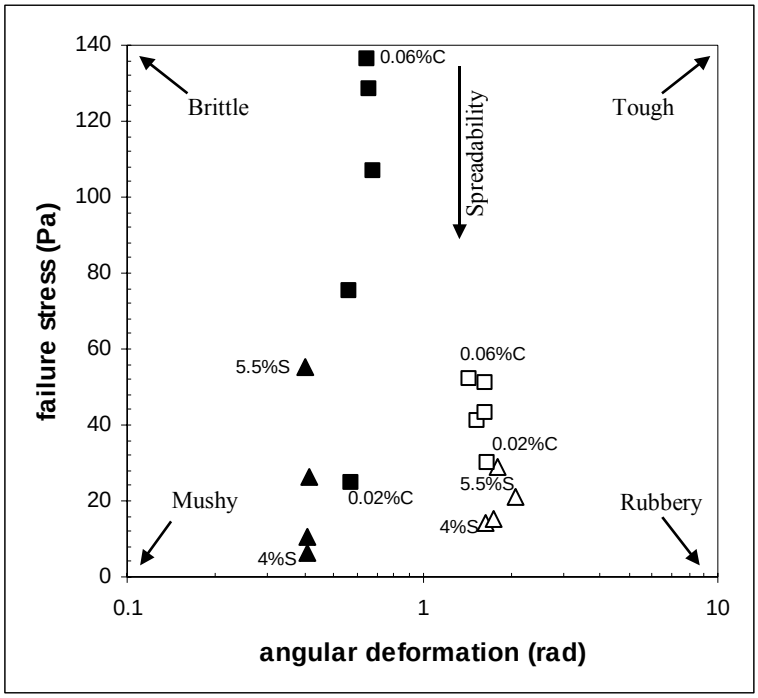

Figure 8. Texture map for samples containing different starch concentration (triangles) and different carrageenan concentration (squares). Croslinked starch(filled symbols) and Amioca starch (empty symbols).

For both starch types, increasing the starch content or the carrageenan content of samples resulted in a decrease on the spreadability and these effects were higher for crosslinked samples. In the case of crosslinked starch samples, those containing carrageenan showed more "tough" charactrisitcs than samples without carrageenan.

4. Conclusions

Differences in plasticity found between native and cross-linked starch revealed important differences in the structure of the starch–milk systems. For cross-linked systems, the increase of the structure strength with the starch concentration was higher than for native starch systems. The presence of small amounts of λ-carrageenan resulted in a large increase in the structure's strength. The differences in the magnitude of this effect found among samples, containing different starch types, indicated that starch still plays an important role in the structure of this type of systems. The effect of λ-carrageenan addition on the yield stress values can be explained by the sum of two effects: the ability of λ-carrageenan to immobilize water, thus increasing the effective starch concentration, and the formation of a λ-carrageenan-casein network, due to the simultaneous presence of λ-carrageenan and casein in the continuous phase.

Acknowledgements

To MEC of Spain for financial support (Project AGL 2003-0052), for the fellowship and for the aid to stay in Cornell University awarded to author Tárrega. To National Starch and Chemical Co, NJ, USA and Degussa Texturant Systems, NE, USA for providing free samples of the materials. To Dr. Luis Durán for his invaluable advice.

References

Acquarone V.M. and Rao, M. A. (2003) Influence of sucrose on the rheology and granule size of cross-linked waxy maize starch dispersions heated at two temperatures. *Carbohydrate Polymers* **51**: 451-458

Alloncle M., and Doublier J.L. (1991). Viscoelastic properties of maize starch/hydrocolloids pastes and gels. *Food Hydrocolloids* **5**: 455-467.

Barnes H.A. and Nguyen Q.D. (2001) Rotating vane rheometry: A review. J. *Non-Newtonian Fluid Mechanics* **98**:1-14

Barnes H.A. and Walters K. (1985) The yield stress myth?. *Rheological Acta* **24**:323-326

Batista, P., Nunes, M. C. and Sousa, I. (2002). Physical characterisation of commercial dairy desserts. In F.J.Martínez Boza, A. Guerrero, P.Partal, J.M. Franco and J. Muñoz (eds)., *Progress in Rheology Theory and Applications* Sevilla: Publicaciones Digitales S.A. pp. 449-452

Briggs J.L., Steffe J.F. and Ustunol Z. (1996). Vane method to evaluate the yield stress of frozen ice cream. Journal of Dairy Science **79**: 527-531

Canet, W. Alvarez M.D. Fernández C.and Luna P. (2005) Comparisons of methods for measuring yield stresses in potato puree: effect of temperature and freezing. *Journal Food Engineering* **68**:143-153

Depypere, F., Verbeken, D., Thas, O. and Dewettinck, K. (2003). Mixture design approach on the dynamic rheological and uniaxial compression behaviour of milk desserts. *Food Hydrocolloids* **17**: 311-320

Genovese D.B. and Rao M.A.(2003). Vane yield stress of starch dispersions. *Journal of Food Science* **68**:2295-2301.

Genovese D.B., Acquarone V.M., Youn K.S. and Rao M.A (2004). Influence of fructose and sucrose on small and large deformation rheological behaviour of heated Amioca dispersions. *Food Science Technology International*, **10**: 51-57

Langendorff V., Cuvelier G., Michon C., Launay B., Parker A. and De Kruif C.G. (2000). Effects of carrageenan type on the behaviour of carrageenan/milk mixtures, *Food Hydrocolloids* **14**: 273–280.

Liu H. and Eskin N.A.M. (1998). Interactions of native and acetylated pea starch with yellow mustard mucilage, locust bean gum and gelatine. *Food Hydrocolloids* **12**, 37-41.

Matser A. M. and Steeneken P.A.M. (1997). Rheological properties of highly cross-linked waxy maize starch in aqueous suspensions of skim milk components. Effects of the concentration of starch and skim milk components. *Carbohydrate Polymers* **32**: 297-305.

Metz B, Kossen N.W.F., and van Suijdam J.C. (1979). The rheology of mould suspensions. In: Ghose TK, Fiechter A, Blakebrough N. (eds), *Advances in Biochemical Engineering*, Vol. 2. New York: Springer Verlag pp. 103-56.

Michaels, A. S. Bolger, J. C. (1962). The plastic flow behavior of flocculated kaolin suspensions. *Industrial Engineering Chemistry Fundamentals* 1: 153-62.

Nayouf M., Loisel C., and Doublier J.L. (2003). Effect of thermomechanical treatment on the rheological properties of crosslinked waxy corn starch. *Journal of Food Engineering* **59**: 209-219.

Nguyen Q.D. and Boger D.V. (1992). Measuring the flow properties of yield stress fluids. *Ann. Rev. Fluid Mech.* **24:** 47–88.

Nguyen Q.D., Jensen, C.T.B. and Kristensen P.G. (1998). Experimental and modelling studies of the flow properties of maize and waxy maize starch pastes. *Chemical Engineering Journal* **70**: 165-171.

Qiu C.G. and Rao, M.A. (1988). Role of pulp content and particle size in yield stress of apple sauce. *Journal of Food Science* **53**:1165-1170.

Rao M.A. and Steffe J.F (1997). Measuring yield stress of fluid foods. *Food Technology* **51**: 50–52.

Shchipunov Y.A and Chesnokov A.V (2003). Carrageenan gels in skim milk: Formation and rheological properties. *Colloid Journal* **65**: 105-113

Tárrega A., Vélez-Ruiz J.F. and Costell E. (2005b). Influence of milk on the rheological behaviour of cross-linked waxy maize and tapioca starch dispersions. *Food Research International* **38**: 759-768

Tárrega, A., Durán, L. and Costell E. (2004). Flow behaviour of semisolid dairy desserts. Effect of temperature. *International Dairy Journal* **14**:345-353.

Tárrega, A., Durán, L. and Costell E. (2005a). Rheological characterization of semisolid dairy desserts. Effect of temperature. *Food Hydrocolloids* **19**:133-139.

Tattiyakul, J. and Rao, M.A. (2000). Rheological behavior of cross-linked waxy maize starch dispersions during and after heating. Carbohydrate Polymers **43**:215-222.

Thebaudin J.Y., Lefebvre A.C., and Doublier J.L (1998). Rheology of starch pastes from starches of different origins: Aplications to starch-based sauces. *Lebensmitttel Wissenschaft und Technologie* **31**: 354-360.

Truong V.D., Daubert C.R., Drake M.A. and Baxter S.R. (2002). Vane rheometry for textural characterization of Cheddar cheese: Correlation with other instrumental and sensory measurements. *Lebensmittel-Wissenschaft und -Technologie* **35**: 305–314.

Umadevi S. and Raghavendra M.R. (1987). Effect of hydrocolloids on the rheological properties of wheat starch. *Carbohydrate Polymers* **7**:395-402.

Van Vliet, T. (2002). On the relation between texture perception and fundamental mechanical parameters for liquids and time dependent solids. *Food Quality and Preference* **13**: 227-236

Velez-Ruiz, J.F., González-Tomás, L. and Costell E. (2005) Rheology of dairy custard model systems: influence of milk fat and hydrocolloid type. *European Food Research and Technology* **221**:342-347.

Wischmann, B., Norsker, M. and Adler-Nissen, J. (2002). Food product models developed to evaluate starch as food ingredient. *Nahrung/ Food* **46**: 167-173

INFLUENCE OF MILK ON THE RHEOLOGICAL BEHAVIOUR OF CROSSLINKED WAXY MAIZE AND TAPIOCA STARCH DISPERSIONS

A. Tárrega[1], J. F. Vélez-Ruiz[2] & E. Costell[1]*

[1] Physical and Sensory Properties Laboratory. Instituto de Agroquímica y Tecnología de Alimentos. CSIC.P.O. Box 73. 46100 Burjassot (Valencia). Spain.

[2]Chemical and Food Engineering Department, Universidad de las Américas, Puebla. Santa Catarina Mártir, Cholula, 72820 Puebla, México.

Abstract

The influence of the addition of milk on the pasting behaviour, the flow and the viscoelasticity of dispersions of three medium cross-linking modified starches was studied. Viscosity values registered after heating and after cooling and the increase of viscosity during cooling ran parallel to the increase in starch concentration in both media, and for the same starch level they were higher in milk systems. These increases also depended on the type of starch. All samples exhibited shear-thinning behaviour and most of them showed time dependent flow behaviour (thixotropy or antithixotropy). The substitution of milk for water originated an increase on both yield stress and apparent viscosity at 1s-1 values that was different depending on starch concentration but similar for all starch types. Most samples showed a clear gel-like behaviour, the storage modulus being higher than the loss modulus. Both moduli values increased with starch concentration and were higher in milk systems, also depending on starch type.

Keywords: Starch dispersions, Milk, Pasting behaviour, Flow behaviour, Viscoelastic properties

*Corresponding author. Tel.:+34-96-3900022; Fax: +34-96-3636301.
E-mail address: ecostell@iata.csic.es

1. Introduction

Both native and modified starches show different behaviour during heating and cooling processes, due to differences in composition. Native starch pastes can be considered structurally as biphasic systems with a continuous phase, essentially an aqueous solution of amylose, leached during granule swelling, and a dispersed phase constituted by swollen starch granules (Tecante & Doublier, 1999). Depending on the starch type, its concentration, and the particular thermomechanical treatment, the resultant system will behave as a viscous fluid or a gel (Thebaudin, Lefebvre & Doublier, 1998; Lagarrigue & Alvarez, 2001). Modified starch granules show higher thermomechanical resistance. If the granules remain whole after pasting, the resultant system is an aqueous dispersion whose rheological behaviour mainly depends on the granules' volumetric fraction and on their rigidity or deformability (Nayouf, Loisel & Doublier, 2003). In both types of starch dispersions, the presence of other ingredients, commonly used in formulated foods, such as sucrose (Sikora, Mazurkiewick, Tomasik & Pielichowski, 1999; Acquarone &Rao, 2003), other sugars (Sopade, Halley & Junming, 2004; Chang, Lim & Yoo, 2004) or hydrocolloids (Tecante et al., 1999; Liu, Eskin & Cui, 2003; Mali, Ferrero, Redigonda, Beleia, Grossmann & Zaritzky, 2003; Krüger, Ferrero & Zaritzky, 2003) modify the characteristics of the dispersed phase, thus affecting the system structure, stability and rheological behaviour.

Both native and modified starches are commonly used in dairy products. However, less attention has been paid to the study of milk-starch than to water-starch systems. It is to be expected that the presence of milk may affect the system structure, depending on the nature of the starch. It has been reported that milk-starch systems are more viscous than water-starch ones for the same starch concentration (Descamps, Langevin & Combs, 1986; Abu-Jdayil, Mohameed & Eassa, 2004). Matser & Steeneken (1997) studied

the influence of some skim milk components on the rheological properties of highly cross-linked waxy maize starch suspensions, finding that lactose increased the system storage modulus, what could be attributed to the increase in rigidity of the starch granules. Casein micelles addition also increased the storage modulus (G´) of starch-skim milk systems. According to these authors, their effect on G´, is probably caused by the exclusion of the casein micelles from the swollen starch granules. As a result, the concentration of the milk proteins in the voids between the granules increases. Thebaudin et al. (1998), compared the rheological behaviour of a dairy system (bechamel sauce) with that of an aqueous system, using different types of starch. They concluded that the properties of the starch-based sauces were similar to those of the starch-water systems although slight differences in behaviour were observed between them. In systems with native starches, the starch based sauces showed lower storage moduli than starch-water systems probably due to the fact that the swelling of the starches is limited by the other product´ components. In systems with modified starches, the storage modulus values were of the same order of magnitude for both sauces and water systems. Recently, Abu-Jdayil et al.(2004) studied the effect of milk on native wheat starch dispersions and found that milk addition increased the apparent viscosity, as compared to the aqueous systems, the differences being higher at higher starch concentrations and also at higher milk fat contents.

The “natillas”, semisolid dairy dessert of wide consumption in Spain, are composed of milk, starch, hydrocolloids, sugars, colorants and aromas. Commercial products exhibited a wide range of flow and viscoelastic properties (Tárrega, Durán & Costell, 2004 and 2005). The different types and concentrations of crosslinked starches, presumably present in the analysed commercial samples, could perhaps be responsible in great part for the observed differences in rheological behaviour of these dairy systems.

The objectives of this paper are to analyse the influence of the addition of whole milk (3.12% fat) on the pasting behaviour, the flow and the viscoelasticity of dispersions of three medium cross-linking modified starches, as compared with aqueous dispersions at the same starch concentrations.

2. Materials and methods

2.1. Materials

Three double modified starches (both substituted and crosslinked) (Cerestar Ibérica, Barcelona, Spain) were used in this study: an acetylated waxy maize adipate starch (AMS) (C*Tex® 06201), a hydroxypropylated waxy maize di-starch phosphate (HMS) (C*PolarTex® 06741), and a hydroxypropylated tapioca di-starch phosphate (HTS) (C*CreamTex® 75720). They are of medium crosslinking level and commonly used for dairy desserts formulations because of their water binding and mouthfeel properties.

The starches were dispersed in two media: water and milk. Water dispersions were prepared by using deionised water; whereas milk dispersions were prepared in whole milk (3.12% fat), both at the following starch concentrations: 2, 3, 4, 5, 6 and 7% (w/w). Whole milk was prepared 24 h in advance by dissolving 12% (w/w) milk powder (Central Lechera Asturiana, Asturias, Spain) in deionised water.

2.2. Starch pasting procedure

A Rapid Visco-Analyser (RVA) instrument (Newport Scientific, Warriewood, Australia) was utilized to evaluate pasting properties of starch dispersions. Thermal treatment and stirring of starch (2 to 7% w/w)

dispersions, in water and in milk, were applied on 25 g samples, placed inside a disposable aluminium canister provided with a plastic stirring paddle. RVA Custard Powder Pasting Method (Method 20, version 5) (Newport Scientific, 1998) was applied as follows: Each sample was rapidly stirred at 960 rpm for 10 s, heating at 50ºC, then the shear input was switched to 160 rpm for the rest of the process. Temperature was held at 50ºC up to 1 min. Then the samples were heated from 50ºC to 95ºC during 3 min 42 s, and the temperature held at 95ºC for 5 min. They were cooled down to 30ºC in 5 min and 48 s, and then held at 30ºC for 4 min 30 s. Viscosity and temperature data were recorded over time; data gathering and analysis were performed using the Thermocline for Windows software, provided by the instrument's manufacturer. Each analysis was done in duplicate.

From the viscosity profiles, three parameters were obtained: the viscosity value registered at the end of the heating period (η_{EH}) (approximately at the tenth minute); the slope of the variation of the viscosity versus cooling time (S), taken at the selected time range of 720 to 1080 s, and the viscosity value at the end of the cooling period (η_{EC}) as the last registered value.

2.3. Rheological measurements

After the thermo-mechanical or preparation process, the starch pastes were kept at 4-5 ºC for 24 hours. Then both the flow and the viscoelastic behaviour of each system were measured.

Measurements were carried out in a controlled stress rheometer RS1 (Thermo Haake, Karlsruhe, Germany), using a serrated parallel plates geometry of 6 cm diameter and 1mm gap, monitored by a RheoWin software package (version 2.93, Haake). A temperature of 5 ±1ºC, selected as representative of the usual consumption temperature of dairy desserts, was

kept during measurements with Phoenix P1 Circulator device (Thermo Haake). Samples were allowed to rest for 15 minutes before measurement and a fresh sample was loaded for each measurement.

Flow behaviour. Starch systems flow was measured by recording shear stress values when shearing the samples at linear increasing shear rates from 1 to 200 s^{-1} through 60 s and down in reverse sequence through the same time. Data from the descending segment of the shear cycle were fitted to Herschel-Bulkley model (Eq. 1) using the Rheowin Pro software (version 2.93, Haake).

$$\sigma = \sigma_0 + K\dot{\gamma}^n \qquad (1)$$

where σ_0 (Pa) is the yield stress, K ($Pa.s^n$) is the consistency index and n is the flow index. In order to fit experimental data to this model a predetermined yield stress value is required (Holdsworth, 1993). In this case, yield stress (σ_0) value was previously obtained by fitting the experimental data to the Casson model (Eq. 2) and calculating the square of the ordinate intercept in the Casson plot (Costell, Carbonell, & Durán, 1993; Skriver, Roemer, & Qvist, 1993).

$$\sigma^{0.5} = \sigma_0^{0.5} + K\dot{\gamma}^{0.5} \qquad (2)$$

Since parameter K units depend on n values, apparent viscosity values at $1s^{-1}$ (η_1) (Eq.3) were used to compare samples consistency.

$$\eta_1 = \sigma_0 + K \qquad (3)$$

Viscoelastic properties. In order to determine the linear viscoelastic region, stress sweeps were run at 1 Hz. The frequency sweeps were performed over the range f = 0.01-10 Hz and the values of the storage modulus (G'), the loss modulus (G''), the loss tangent angle (tan δ) and the complex viscosity (η*),

as a function of frequency, were calculated using the Rheowin Pro software (version 2.93, Haake).

2.4. Statistical analysis

The effects of starch type, starch concentration and dispersion medium on the three parameters obtained from the viscosity profile, registered during starch pasting procedure ($\eta_{EH,}$ S and η_{EC}), on the flow parameters ($\sigma_{0,}$ η_1 and n) and on the viscoelastic parameters (G', G'', tan δ and η*) were analysed by ANOVA including three factors with interactions. The Fisher test (α=0.05) was used to calculate the minimum significant difference. All calculations were carried out with the Statgraphics Plus 4.1 software.

3. Results

3.1. Viscosity-temperature profiles

Viscosity-temperature profiles of water-starch systems with the lower starch concentrations (2 and 3%) did not show any response during the pasting procedure, behaving as dilute solutions. The dilute solution behaviour in water-starch systems can be a result of the combined effects of low starch concentration and of undercooking of the starch granules during the thermal treatment applied. As stated by Nayouf et al., (2003), in the dilute regime, the volume fraction of swollen particles is so low that there is almost no contact between starch granules. In this situation the dispersion viscosity during pasting procedure could remain practically unaltered. Furthermore, after 24 h of storage at 4-5ºC, a clear syneresis was observed in these samples and a transparent, aqueous layer over a turbid gel-like phase was detected. A similar effect was observed by Zimeri & Kokini (2003) in inulin-waxy maize starch systems for samples in which the starch concentration

was below the critical concentration. The dilute solution condition and the phase separation observed in the above mentioned samples did not permit the study of their rheological behaviour. Except for sample with 7% AMS in milk, which developed a unique decreasing trend at the last five minutes of processing, and its final viscosity (4.293 Pa s) was lower than the corresponding viscosity at 15 minutes (5.740 Pa s), all of the viscosity profiles of the other studied systems showed a similar pattern. The viscosity increased during the heating period at constant temperature (95ºC), continued to increase during cooling and the profile finalized with a plateau region, corresponding to the particular final viscosity for each model system. As an example, viscosity profiles, obtained for 6% starch (HMS, HTS and AMS) dispersions, in the two dispersion media, water and milk, are shown in Figure 1. Some differences in the swelling temperature, taken as that at which consistency began to increase, were observed. This temperature varied from 62.0 to 70.4ºC in water-starch systems and from 67.1 to 74.3ºC in milk-starch systems. The viscosity value registered at the end of heating period (η_{EH}) (Table 1), and the viscosity value at the end of cooling period (η_{EC}) (Figure 2), obtained from the viscosity profiles of the studied starch dispersions, were compared. For the three studied starches, η_{EH} and η_{EC} values increased with starch concentration, due to the increase in the volumetric fraction of the starch granules in the dispersion. At the same starch concentration, both parameters showed higher values for milk dispersions, attributable to the higher viscosity of the dispersing phase, due to the presence of caseins, lactoglobulins, fat and the other milk components (Vélez-Ruiz & Barbosa, 1997) and to the possible interactions between these components and starch

(Matser et al. ,1997; Abu-Jdayil et al. 2004). In all samples , the viscosity profile during the cooling time between 720 and 1080 s was fitted to a linear equation (R^2>0.972) and the slope (S) of the line was obtained (Table 1).

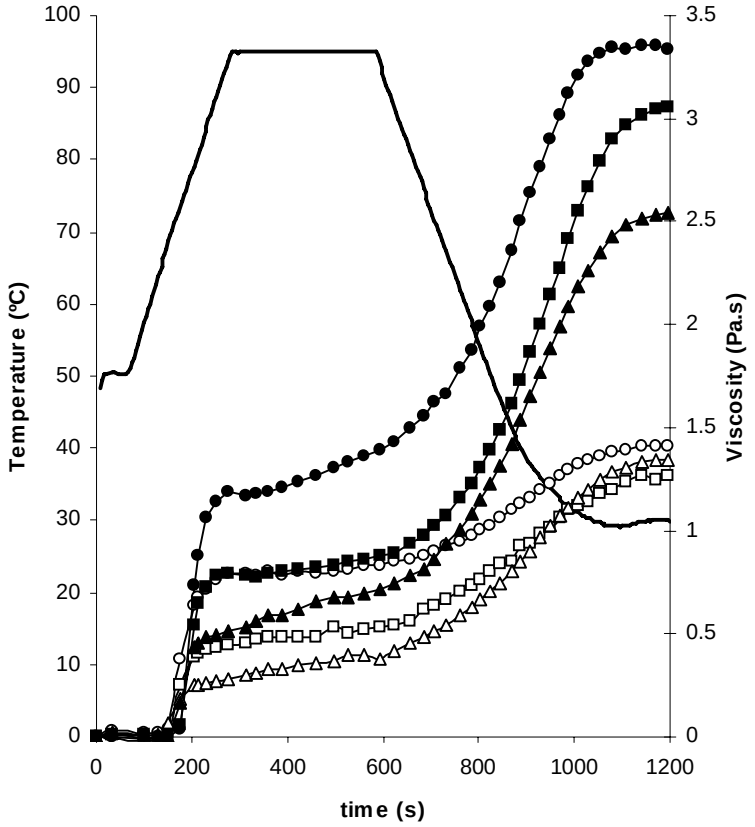

Figure 1. Viscosity profiles during thermal treatment of 6% HMS (squares), HTS (triangles) and AMS (circles) starch dispersions in water (open symbols) and in milk (filled symbols). Identification of starch type in table1. Temperature profile (—).

Table 1. Viscosity values registered at the end of the heating period (η_{EH}) and slope of viscosity versus cooling time (S) for water and milk starch dispersions at different concentrations of the three starch types[a]

Starch type[b]	Starch Concentration(%)	Water		Milk	
		η_{EH} (Pa.s)	S	η_{EH} (Pa.s)	S
HMS	2	-	-	0.003 (0.002)	0.026 (0.030)
	3	-	-	0.013 (0.001)	0.159 (0.005)
	4	0.013 (0.016)	0.152 (0.013)	0.038 (0.004)	0.723 (0.086)
	5	0.142 (0.001)	0.667 (0.011)	0.241 (0.026)	2.017 (0.037)
	6	0.548 (0.020)	1.695 (0.636)	0.898 (0.028)	5.803 (0.147)
	7	1.265 (0.115)	3.842 (0.124)	2.087 (0.072)	11.44 (0.049)
HTS	2	-	-	0.004 (0.001)	0.054 (0.016)
	3	-	-	0.026 (0.006)	0.103 (0.004)
	4	0.034 (0.020)	0.120 (0.031)	0.046 (0.002)	0.498 (0.042)
	5	0.077 (0..016)	0.704 (0.010)	0.179 (0.012)	1.799 (0.056)
	6	0.387 (0.019)	2.409 (0.180)	0.736 (0.024)	4.812 (0.150)
	7	1.181 (0.067)	5.641 (0.297)	2.044 (0.006)	9.013 (0.260)
AMS	2	-	-	0.020 (0.019)	0.019 (0.014)
	3	-	-	0.044 (0.008)	0.221 (0.077)
	4	0.080 (0.016)	0.207 (0.013)	0.124 (0.029)	0.891 (0.037)
	5	0.346 (0.009)	0.681 (0.037)	0.511 (0.028)	2.311 (0.021)
	6	0.830 (0.003)	1.516 (0.107)	1.401 (0.005)	5.907 (0.662)
	7	1.454 (0.15)	3.157 (0.167)	3.433 (0.175)	3.661 (0.128)

a. Mean values and standard deviations (in parenteses) of duplicate measurements

b. Identification of starch type:
HMS: hydroxypropylated waxy maize di-starch phosphate
AMS: acetylated waxy maize adipate starch
HTS: hydroxypropylated tapioca di-starch phosphate

The increase in viscosity during cooling, as represented by parameter S, ran parallel to the increase in starch concentration in both media. For the same starch level S was higher in milk systems. For intermediate starch concentration samples (4, 5 and 6%), the effect of the ternary interaction (type of starch, starch concentration and dispersing medium) on $\eta_{EH,}$ S, and η_{EC} values was significant (Table 2), what means that the effect of milk addition on all three parameters depended on both starch type and concentration.

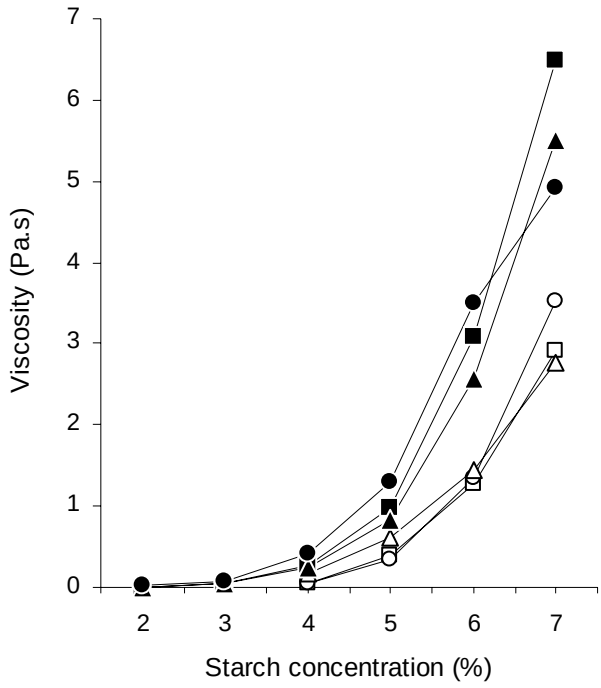

Figure 2. Viscosity values at the end of the cooling period (η_{EC}) of: HMS (□), HTS (△) and AMS (○) starch dispersions in water (open symbols) and in milk (filled symbols). Identification of starch type in table1.

Table 2. Effects of medium (water or milk), starch concentration and starch type on values of the parameters obtained from the viscosity profiles of the three starch types at 4, 5 and 6% starch concentrations. F and p values.

	η_{EH}		S		η_{EC}	
	F	p	F	p	F	p
Main effects						
Medium	986.15	0.0000	952.49	0.0000	2442.24	0.0000
Starch Concentration	5389.68	0.0000	1050.49	0.0000	5040.73	0.0000
Starch Type	926.35	0.0000	3.61	0.0479	140.50	0.0066
Binary Interactions						
Medium x Starch Concentration	387.06	0.0000	239.13	0.0000	702.60	0.0000
Medium x Starch Type	32.63	0.0000	22.62	0.0030	42.09	0.0000
Starch Type x Starch Concentration	187.87	0.0000	0.36	0.0833	13.17	0.0000
Ternary Interactions						
Medium x Starch Type x Starch Concentration	10.77	0.0001	8.15	0.0006	18.09	0.0000

3.2. Flow behaviour

Rheograms (up- and downward curves) of samples containing 4, 5, 6 and 7% starch in water and 2, 3, 4, 5 and 6% starch in milk were recorded for each type of starch. All samples exhibited shear thinning behaviour. As an example rheograms obtained for 4% starch dispersions are shown in Figure 3. Samples with starch concentrations over 4% in water systems and over 2% in milk systems showed time-dependent flow. All of these were thixotropic, except 6% maize starch (HMS and AMS) aqueous samples which showed antithixotropic behaviour (Figure 4).

Time dependence of starch pastes has been reported by several authors. Nguyen, Jensen and Kristensen (1998) found that both normal and waxy maize starch dispersions were thixotropic and Tecante et al. (1999) and Nayouf et al.(2003) observed an antithixotropic behaviour in the flow of crosslinked waxy corn starch pastes. The latter authors interpreted that antithixotropic behaviour would be explained by a rearrangement of the starch granules, enhanced by shearing. Tattiyakul & Rao (2000) observed

that a 5% cross-linked starch dispersion exhibited combined hysteresis loops. The antithixotropic behaviour appeared at low shear rates and the thixotropic behaviour at higher shear rates. They observed that for this starch concentration, at temperatures from 20 to 80ºC, the shear stress limits between the different kinds of time dependence appeared at a shear stress range between 120 and 150 Pa, and that beyond this range, the sample showed thixotropic behaviour.

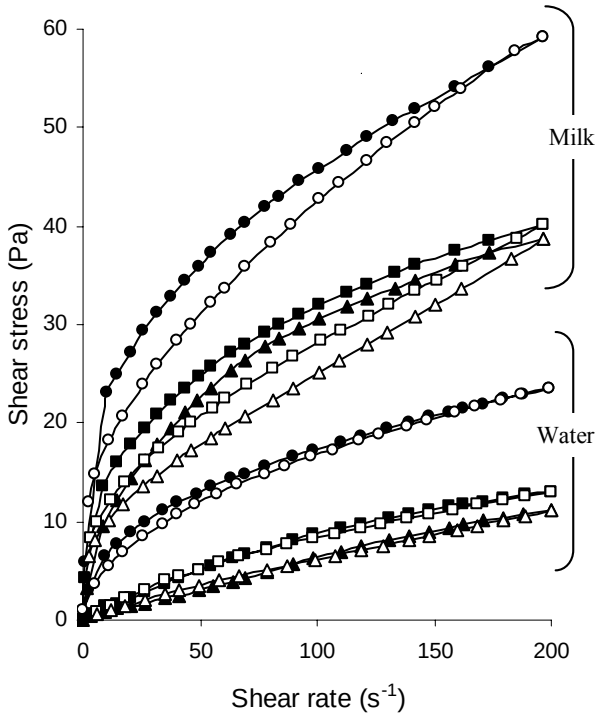

Figure 3. Flow behaviour of 4% starch pastes in water and in milk. Up-curve (filled symbols) and down-curve (open symbols). HMS (□), HTS (△) and AMS (○). Identification of starch type in table1.

In the present study, the shear stress imposed to the 6% cross-linked maize and tapioca starch water dispersions was less than 160-180 Pa, when they were sheared in the range 1-200-1 s^{-1} (Figure 4). Only the samples containing maize starch showed antithixotropy, indicating that the time

dependent behaviour of starch dispersions depends not only on the starch concentration and on the shear conditions, but also on the starch type.

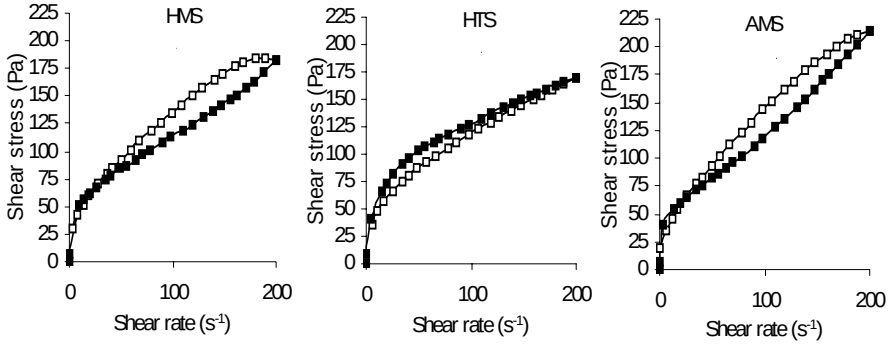

Figure 4. Flow behaviour of 6% starch pastes in water. Up-curve (filled symbols) and down-curve (open symbols). Identification of starch type in table1.

In general, substitution of milk for water in the studied systems originated an increase in the registered shear stress and in the hysteresis loop area. The two samples showing antithixotropy in water showed thixotropy in the milk systems. These results could be attributed to the higher rigidity of starch granules in milk dispersions (Matser et al., 1997; Abu-Jdayil et al., 2004).

Characterisation of the flow behaviour of samples was done from the experimental data obtained in the downward rheogram. Flow data were fitted to the Herschel-Bulkley model obtaining R^2 values between 0.9868 and 0.9998 (Figure 5). As expected, in both water and milk starch dispersions the consistency coefficient (K) and the yield stress (σ_0) values increased with starch concentration while the flow index (n) values slightly decreased, this indicating an increase in shear-thinning behaviour. It should be noted that both K and σ_0 increments were relatively smaller for AMS than for the other two starches (Table 3).

Table 3. Herschel-Bulkley fit of starch pastes in water and in milk at 5ºC. Flow parameters values.[a]

Starch type[b]	Starch (%)	Water			Milk		
		σ_0 [c] (Pa)	K_{HB} (Pa.s^n)	n_{HB}	σ_0 [c](Pa)	K_{HB} (Pa.s^n)	n_{HB}
HMS	2	-	-	-	0.63 (0.05)	0.11 (0.004)	0.66 (0.0003)
	3	-	-	-	2.26 (0.04)	0.32 (0.002)	0.64 (0.0061)
	4	0.52 (0.19)	0.21 (0.05)	0.76 (0.020)	7.20 (0.19)	1.08 (0.03)	0.65 (0.0031)
	5	8.99 (1.21)	1.57 (0.06)	0.62 (0.002)	28.37 (0.31)	4.52 (0.08)	0.65 (0.0053)
	6	28.64 (0.43)	5.69 (0.05)	0.67 (0.003)	89.61 (0.44)	11.51 (0.13)	0.61 (0.0156)
	7	52.74 (2.22)	11.26 (0.24)	0.68 (0.004)	-	-	-
HTS	2	-	-	-	0.19 (0.17)	0.05 (0.03)	0.76 (0.0636)
	3	-	-	-	1.72 (0.34)	0.29 (0.05)	0.68 (0.004)
	4	0.14 (0.00)	0.12 (0.01)	0.86 (0.003)	5.07 (0.40)	0.91 (0.06)	0.69 (0.002)
	5	6.00 (0.16)	1.32 (0.01)	0.69 (0.003)	23.10 (3.34)	3.68 (0.57)	0.68 (0.003)
	6	29.83 (1.53)	4.69 (0.18)	0.65 (0.003)	86.87 (4.73)	11.28 (0.78)	0.65 (0.0009)
	7	97.49 (0.16)	12.86 (0.19)	0.62 (0.003)	-	-	-
AMS	2	-	-	-	0.72 (0.08)	0.12 (0.008)	0.65 (0.003)
	3	-	-	-	2.92 (0.04)	0.41 (0.001)	0.64 (0.001)
	4	2.88 (0.55)	0.58 (0.12)	0.66 (0.120)	9.59 (1.8)	1.43 (0.25)	0.65 (0.0004)
	5	11.46 (1.29)	1.90 (0.24)	0.64 (0.003)	27.79 (4.39)	4.44 (0.55)	0.65 (0.007)
	6	19.89 (0.00)	4.58 (0.21)	0.71 (0.004)	74.38 (3.59)	9.27 (0.14)	0.61 (0.015)
	7	37.51 (2.39)	7.86 (0.41)	0.70 (0.006)	-	-	-

a. Mean values and standard deviations (in parenteses) of duplicate measurements
b. Identification of starch type in Table 1
c.Yield stress (σ_0) calculated by fitting experimental data to the Casson model ($\sigma^{0.5}=\sigma_0^{0.5}+K\gamma^{0.5}$)

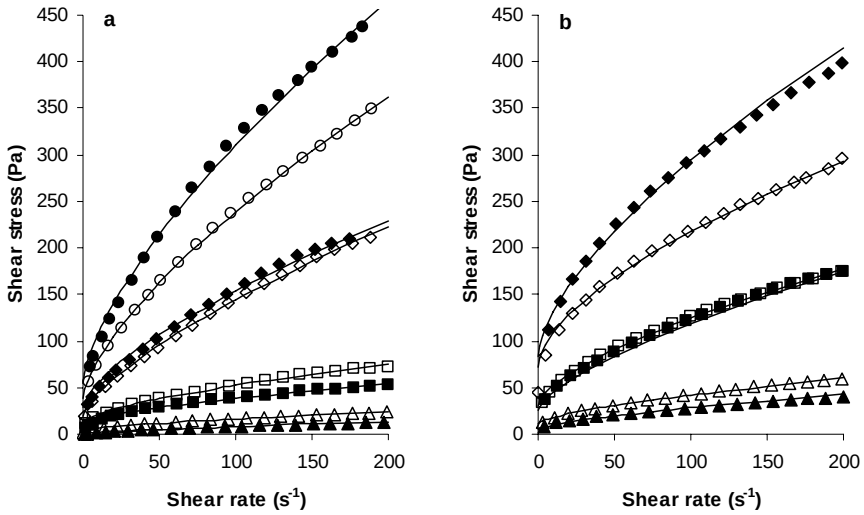

Figure 5. Downward rheograms of starch pastes in water (a) and in milk (b) for two starch types: HMS (filled symbols) and AMS (open symbols). Starch concentrations: 4% (△) 5% (□) 6% (◇) and 7% (○). Fits to Herschel-Bulkey model (—). Identification of starch type in table 1.

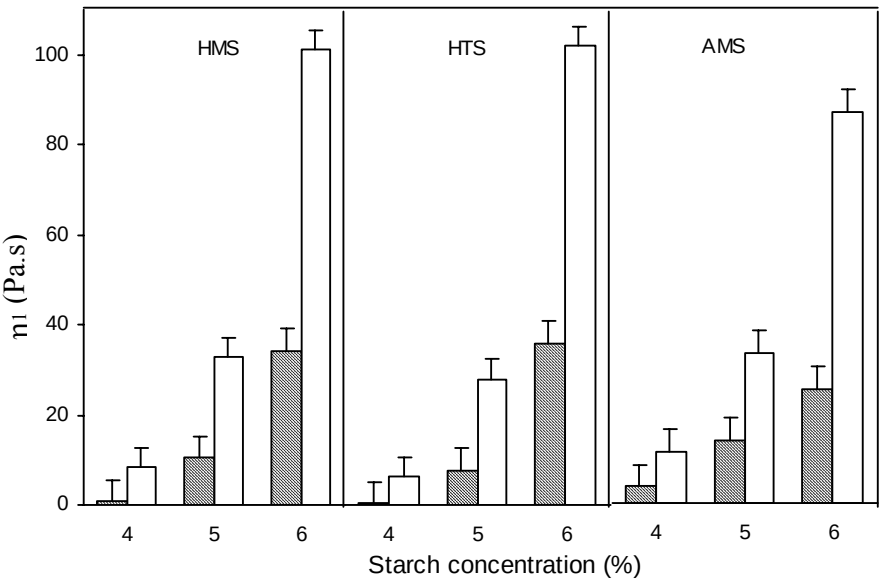

Figure 6. Values of apparent viscosity at 1 s^{-1} of starch pastes in water (▨) and in milk (▭). Identification of starch type in table1.

A three-way ANOVA with interactions was used to study the combined effects of the type of medium (water or milk), the type of starch (HMS, HTS, AMS) and the starch concentration (4, 5, and 6%) on the variations of yield stress (σ_0), apparent viscosity at $1s^{-1}$ (η_1) and flow index (n). Only for n values the ternary interaction was significant ($\alpha \leq 0.05$), showing that all three factors affected the systems pseudoplasticity.

Table 4. Effects of medium, starch concentration and starch type on values of the flow behaviour parameters of starch pastes at 4, 5 and 6% starch concentrations. F and p values.

	σ_0		n		η_1	
	F	p	F	p	F	p
Main effects						
Medium	1571.45	0.0000	309.84	0.0000	1557.14	0.0000
Starch Concentration	1968.27	0.0000	211.94	0.0000	2042.68	0.0000
Starch Type	6.33	0.0083	136.33	0.0000	6.72	0.0066
Binary Interactions						
Medium x Starch Concentration	519.98	0.0000	132.92	0.0000	494.61	0.0000
Medium x Starch Type	2.07	0.1554	8.17	0.0030	2.06	0.1567
Starch Type x Starch	23.37	0.0000	73.68	0.0000	23.45	0.0000
Ternary Interactions						
Medium x Starch Type x Starch Concentration	0.66	0.6256	70.43	0.0000	0.80	0.5404

For the other two parameters the type of medium-starch concentration interaction was significant and the type of medium-type of starch interaction was not so, indicating that the effect of substituting milk for water on both plasticity (σ_0 values) and apparent viscosity (η_1 values) was different, depending on starch concentration, but similar for all starch types. Apparent viscosity was higher in milk than in water systems, the increment being larger, the higher the starch concentration (Figure 6). These results followed the same trend than those obtained by Matser & Steeneken (1997) and by Abu-Jdayil et al. (2004). The latter authors also observed that the apparent

viscosity of 6% wheat starch pastes at 2.2 s^{-1} increased by 5% using low fat (1.5 %) milk and by 15% using high fat (3 %) milk, compared with using skim milk (0.2% fat), and concluded that besides the effect of milk on the increase in rigidity of the starch granules, the three-dimensional fat polymers contributed to the increase in apparent viscosity of starch milk pastes.

3.3. Viscoelastic properties

Stress sweeps of 4, 5, 6 and 7% starch dispersions in water and 2, 3, 4, 5, 6 and 7% starch dispersions in milk were carried out with some exceptions: 4% HTS water sample, 2% HMS and 2% HTS milk samples mechanical spectra could not be obtained with the equipment used (linear viscoelasticity zone could not be registered). As expected the viscoelastic characteristics of both water and milk dispersions of the three starches studied mainly depended on the starch concentration and on the nature of the dispersing medium. Both the 4% HMS (Figure 7a) and the 5% HTS aqueous dispersions showed moduli values dependent on frequency, G'' values being higher than G' ones, indicating fluid behaviour. The rest of samples showed a clear gel-like behaviour, G´ being higher than G´´.

For comparison purposes, G', G'', tan δ and η∗ values at a frequency of 1 Hz were considered (Table 5). In general, both storage and loss moduli increased and loss angle tangent decreased with starch concentration, indicating an increase in the relative elastic contribution to the aqueous dispersions viscoelasticity. G' and G'' values were higher in milk systems but the variations observed in tan δ values depended on both starch type and concentration. Only in the case of HTS starch, tan δ showed a decrease when milk was added. Complex viscosity increased with starch concentration and on substituting milk for water. However, the increments in this parameter, due to starch concentration, were smaller in the case of AMS starch,

similarly to the variations observed for parameters σ_0 and η_1, as previously reported.

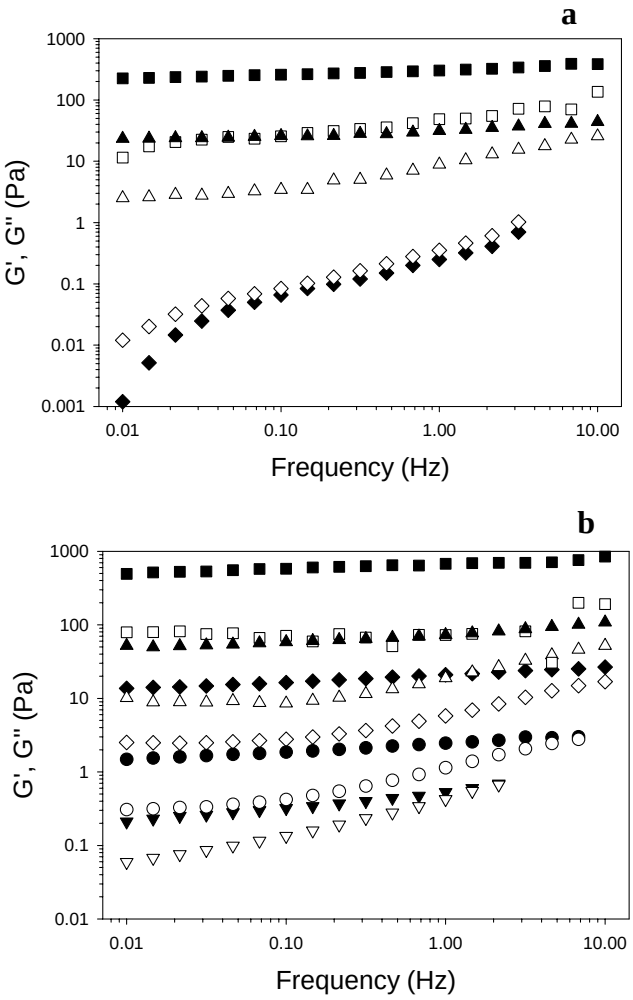

Figure 7. Mechanical spectra for hydroxypropylated waxy maize di-starch phosphate (HMS) in water (a) and in milk (b). Starch concentration: 2% (▽), 3% (○), 4% (◇), 5%(△), and 7% (□). G' (filled symbols) and G'' (open symbols).

Table 5. Storage modulus (G'), loss modulus (G''), loss angle tangent (tan δ) and complex viscosity (η∗) values at 1 Hz for starch pastes at 5ºC [a].

Starch type[b]	C(%)	Water				Milk			
		G'(Pa)	G''(Pa	tan δ	η∗(Pa.s	G'(Pa)	G''(Pa	tanδ	η∗(Pa.s
HMS	2	-	-	-	-	-	-	-	-
	3	-	-	-	-	2.82 (0.51)	1.26 (0.18)	0.45 (0.125	0.49 (0.86)
	4	0.16 (0.13)	0.27 (0.11)	2.15 (1.04)	0.05 (0.03)	24.80 (5.52)	6.63 (1.21)	0.27 (0.007	4.09 (0.90)
	5	31.1 (0.42)	8.025 (1.24)	0.26 (0.37)	5.11 (0.11)	77.30 (6.08)	20.06 (1.60)	0.26 (0.00)	12.71 (1.00)
	6	171.00 (16.97)	28.35 (2.91)	0.17 (0.00)	27.60 (2.70)	297.50 (3.53)	70.60 (3.71)	0.20 (0.007	48.71 (0.71)
	7	311.50 (12.02)	49.86 (1.99)	0.16 (0.00)	50.22 (1.92)	702.00 (36.77)	77.16 (6.12)	0.11 (0.002	112.40 (5.94)
HTS	2	-	-	-	-	-	-	-	-
	3	-	-	-	-	2.21 (0.13)	1.37 (0.01)	0.62 (0.028	0.41 (0.016)
	4	-	-	-	-	9.69 (3.27)	4.85 (1.14)	0.51 (0.039	1.73 (0.55)
	5	2.56 (0.95)	2.342 (0.48)	0.94 (0.16)	0.55 (0.16)	83.10 (8.34)	34.98 (4.31)	0.42 (0.007	14.35 (1.48)
	6	110.00 (11.31)	30.43 (2.57)	0.28 (0.01)	18.125 (1.86)	472.50 (6.36)	95.91 (4.87)	0.20 (0.009	76.79 (0.83)
	7	258.50 (16.26)	68.72 (3.74)	0.27 (0.001	42.54 (2.59)	800.50 (30.41)	103.93 (8.44)	0.13 (0.004	128.55 (5.02)
AMS	2	-	-	-	-	1.545 (0.95)	0.88 (0.51)	0.58 (0.017	0.28 (0.17)
	3	-	-	-	-	5.195 (0.69)	1.50 (0.15)	0.29 (0.007	0.86 (0.11)
	4	8.37 (1.29)	1.60 (0.08)	0.192 (0.02)	1.36 (0.20)	25.65 (3.75)	5.70 (0.79)	0.22 (0.001	4.19 (0.61)
	5	64.60 (7.78)	8.38 (1.16)	0.13 (0.00)	10.36 (1.25)	92.15 (0.92)	23.09 (0.44)	0.25 (0.005	15.12 (0.12)
	6	145.50 (17.68)	18.97 (2.40)	0.13 (0.00)	23.37 (2.90)	260.00 (45.25)	43.19 (6.02)	0.17 (0.004	41.88 (7.25)
	7	241.50 (33.23)	30.20 (3.78)	0.13 (0.00)	38.69 (5.32)	382.00 (4.24)	42.00 (5.93)	0.11 (0.010	61.18 (0.68)

a. Mean values and standard deviations (in parenteses) of duplicate measurements
b. Identification of starch type in Table 1

An analysis of variance of three factors (starch type, starch concentration and type of medium) with interactions applied to the values of G', G'', tan δ and ηP^* at 1 Hz, corresponding to 5, 6 and 7% starch dispersions, both in water and in milk, showed that the ternary interaction was significant for all parameters (Table 6), indicating that the three factors considered contributed to the viscoelastic properties of the studied dispersions.

Table 6. Effects of medium, starch concentration and starch type on the values of G', G'', tanδ and η* at 1Hz of starch pastes at 5, 6 and 7% starch concentrations. F and p values.

	G'		G''		tan δ		η*	
	F	p	F	p	F	p	F	p
Main effects								
Medium	9.84	0.0000	22.39	0.0002	478.02	0.0000	981.56	0.0000
Starch Concentration	1213.37	0.0000	106.8	0.0000	403.26	0.0000	1191.90	0.0000
Starch Type	69.87	0.0000	101.6	0.0000	147.74	0.0000	73.92	0.0000
Binary Interactions								
Medium x Starch Concentration	186.03	0.0000	9.79	0.0013	29.84	0.0000	176.58	0.0000
Medium x Starch Type	110.22	0.0000	46.87	0.0000	35.41	0.0030	108.81	0.0000
Starch Type x Starch Concentration	53.22	0.0000	42.17	0.0000	35.54	0.0000	52.73	0.0000
Ternary Interaction								
Medium x Starch Type x Starch Concentration	26.06	0.0000	16.15	0.0000	3.49	0.0281	24.50	0.0000

It can then be concluded that although the rheological behaviour of cross-linked starch dispersions, prepared following the same thermomechanical treatment, mainly depended both on the type of starch and on the granules volumetric fraction, the changes in the characteristics of the dispersing medium, due to substitution of milk for water, clearly altered their

rheological properties. Such effect could be attributed to the increase in the starch granules rigidity and to the fact that some milk components, like caseine or fat, may affect the whole system structure.

Acknowledgements

To MCyT of Spain for financial support (Project AGL 2003-0052) and for the fellowship awarded to author Tárrega. To Universidad de las Américas of Mexico for financial support awarded to author Vélez-Ruiz. To Dr. Luis Durán for his valuable contribution.

References

Abu- Jdayil, B., Mohameed, H. & Eassa, A. (2004). Rheology of wheat starch-milk-sugar systems: effect of starch concentration, sugar type and concentration, and milk fat content. *Journal of Food Engineering*, 64, 207-212.

Acquarone, V. M., and Rao, M. A. (2003) Influence of sucrose on the rheology and granule size of cross-linked waxy maize starch dispersions heated at two temperatures, *Carbohydrate Polymers,* 51, 451-458.

Costell, E. Carbonell, E., & Durán, L. (1993). Rheological indices of fruit content in jams: effect of formulation on flow plasticity of sheared strawberry and peach jams. *Journal of Texture Studies*, 24, 375-390.

Descamps, O., Langevin, P., & Combs, D.H. (1986). Physical effect of stach/carrageenan interactions in water and milk. Food Technology, 40, 81-88.

Holdsworth, S. D. (1993). Rheological models used for the prediction of the flow properties of food products. *Transactions of the Institution of Chemical Engineers*, 71, 139-179.

Krüger, A., Ferrero, C. & Zaritzky, N. E. (2003). Modelling corn starch swelling in batch systems: effect of sucrose and hydrocolloids. *Journal of Food Engineering*, 58, 125-133.

Lagarrigue, S. and Alvarez, G. (2001). The rheology of starch dispersions at high temperatures and high shear rates: A review. *Journal of Food Engineering*, 50, 189–202.

Liu, H., Eskin, N. A. M & Cui, S. W. (2003). Interactions of wheat and rice starches with yellow mustard mucilage. *Food Hydrocolloids*, 17, 863-869.

Mali, S., Ferrero, C., Redigonda, V., Beleia, A. P., Grossmann, M. V. E. & Zaritzky, N. E. (2003). Influence of pH and hydrocolloids addition on yam (Dioscorea alata) starch pastes stability. *Lebensmitttel Wissenschaft und Technologie*, 36, 475-481.

Matser, A. M. & Steeneken, P. A. M. (1997). Rheological properties of highly cross-linked waxy maize starch in aqueous suspensions of skim milk components. Effects of the concentration of starch and skim milk components. *Carbohydrate Polymers*, 32, 297-305.

Nayouf, M., Loisel, C., & Doublier, J. L. (2003). Effect of thermomechanical treatment on the rheological properties of crosslinked waxy corn starch. *Journal of Food Engineering*, 59, 209-219.

Nguyen, Q. D., Jensen, C. T. B., & Kristensen P. G. (1998). Experimental and modelling studies of the flow properties of maize and waxy maize starch pastes. *Chemical Engineering Journal*, 70, 165-171.

Sikora, M., Mazurkiewicz, J., Tomasik, P. & Pielichowski, K., (1999). Rheological properties of some starch–water–sugar systems. *International Journal of Food Science and Technology*, 34, 371–383.

Skriver, A., Roemer, H., & Qvist, K. B. (1993). Rheological characterization of stirred yoghurt; viscometry. *Journal of Texture Studies*, 24, 185-198.

Sopade, P. A. Halley, P. J. & Junming, L. L. (2004).Gelatinisation of starch in mixtures of sugars. I. Dynamic rheological properties and behaviours of starch–honey systems. *Journal of Food Engineering*, 61, 439-448.

Tárrega, A., Durán, L. & Costell, E. (2004). Flow behaviour of semi-solid dairy desserts. Effect of temperature. *International Dairy Journal*, 14, 345-353.

Tárrega, A., Durán, L. & Costell, E. (2005). Rheological characterization of semisolid dairy desserts. Effect of temperature. *Food Hydrocolloids*, 19, 133-139.

Tattiyakul, J.& Rao, M. A. (2000). Rheological behavior of cross-linked waxy mayze starch dispersions during and after heating. *Carbohydrate Polymers*, 43, 215-222.

Tecante, A., & Doublier, J. L.(1999). Steady flow and viscoelastic behavior of crosslinked waxy cornstarch-k-carrageenan pastes and gels. *Carbohydrate Polymers*, 40, 221-231.

Thebaudin, J. Y., Lefebvre, A. C., & Doublier, J. L (1998). Rheology of starch pastes from starches of different origins: Aplications to starch-based sauces. *Lebensmitttel Wissenschaft und Technologie*, 31, 354-360.

Vélez-Ruiz, J.F. & Barbosa-Cánovas, G.V. (1997). Rheological properties of selected dairy products. *Critical Reviews of Food Science and Nutrition*, 37, 311–359.

Zimeri, J.E. & Kokini, J.L. (2003). Rheological properties of inulin–waxy maize starch systems. *Carbohydrate Polymers* 52, 67–85.

EFECT OF COMPOSITION ON THE RHEOLOGICAL BEHAVIOUR AND SENSORY PROPERTIES OF SEMISOLID DAIRY DESSERT

A. Tárrega & E. Costell*

[1]*Instituto de Agroquímica y Tecnología de Alimentos (CSIC). P.O. Box 73, 46100 Burjassot, Spain.*

Abstract

The rheological behaviour and sensory properties of thirty vanilla dairy dessert model systems were studied, with special attention to the effects of λ-carrageenan concentration and milk fat content. The viscosity profiles recorded during the thermo-mechanical process showed differences as a function of sample formulation. The addition of λ-carrageenan resulted in an increment of the registered viscosity values. During cooling the samples containing higher carrageenan concentration reached the maximum value of apparent vicosity at higher temperatures than in the case of samples without carrageenan. Most systems showed a clear gel-like behaviour, except those with the lowest starch concentrations and without carrageenan, that showed fluid-like behaviour. G' values, registered at 1 Hz, increased with carrageenan concentration. For samples with less than 0.1% λ-carrageenan, the presence of milk fat increased G' values and for higher carrageenan concentrations the effect was the opposite. As expected, the thickness perceived, both in the skim milk and in the whole milk dairy desserts, increased with λ-carrageenan concentration. Concentrations of λ-carrageenan up to 0.06% increased creaminess. In general, samples with higher λ-carrageenan concentration were perceived with less flavour intensity and with less sweetness.

Keywords: Dairy desserts, λ-carrageenan, Fat content, Viscoelastic properties, Sensory properties

*Corresponding author. Tel.:+34-96-3900022; Fax: +34-96-3636301.
E-mail address: ecostell@iata.csic.es

1. Introduction

Starch based dairy desserts are basically formulated with milk, thickeners (starch and hydrocolloids), sucrose, aroma and colorants. The rheological and sensory properties of these products are strongly influenced by the particular characteristics of some ingredients, like fat content of milk, type and concentration of starch, and/or type and concentration of hydrocolloids, and their crossed interactions. Both native and modified starches are commonly used in dairy products although the use of modified starches is increasing as they show higher thermomechanical resistance and more stability than native starches producing dairy desserts with more texture and without syneresis (Nadison &Dureau, 1992). In general, it is considered that the most suitable structure-forming hydrocolloids for dairy products are carrageenans, mainly κ- and ι-carrageenan, due to their capability of combining into double helices and to their interactions with casein, forming network structures closely related to the helix-coil transition temperature (de Vries, 2002; Langendorff, Cuvelier, Launay, Michon, Parker & De Kruif, 1999; Spagnuolo, Dalgleish, Goff & Morris, 2005; Michon, Chapuis, Langendorff, Boulenguer & Cuvelier, 2005). Lambda-carrageenan molecules have a strongly anionic charge, due to the presence of three sulphate groups, and it does not form gels in aqueous solutions, causing only an increase in viscosity. However it has been shown that λ-carrageenan is able to form gels in the presence of milk due to their interaction with the casein micelles causing an increase in the micelle size by the adsortion of the carrageenan to the micelles. (Langendorff, Cuvelier, Michon, Launay, Parker & De Kruif. 2000; Shchipunov and Chesnokov, 2003). According to the former authors, λ-carrageenan, although it is not capable of combining into double helices, it shows attractive interactions with casein micelles, that can induce binding of the micelles and formation of a carrageenan/casein network on cooling.

Semisolids dairy desserts show time dependent and shear thinning flow behaviour, and viscoelastic properties typical of weak gels. Noticeable differences in rheological behaviour have been found in commercial samples (Batista, Nunes & Sousa, 2002; Tárrega, Durán & Costell, 2004 and 2005) and in model systems with different compositions (Wischman, Norsker and Alder-Nissen, 2002; Depypere, Verbeken, Thas & Dewettinck, 2003; Nunes, Batista, Raymundo, Alves & Sousa 2003; Lethuaut, Brossard, Rousseau, Bousseau & Genot, 2003; Yang, Irudayaraj, Otgonchimeg & Walsh, 2004; Velez- Ruíz, González-Tomás & Costell, 2005). Recently, Verbeken, Thas & Dewettink (2004) analysed the influence of the composition on the rheological properties of pudding desserts composed of κ- carrageenan, native maize starch, skim milk powder, sucrose and water, and concluded that their rheological behaviour seem to be mainly governed by the exclusion effect of swollen starch granules, thus concentrating κ- carrageenan in the continuous water phase. Less information is available about sensory characteristics of this type of products. De Wijk, van Gemert, Terpstra and Wilkinson (2003), using a trained panel, developed a set of sensory attributes for describing flavour, odour, mouth feel and after feel of commercial vanilla custard desserts. Two main sensory dimensions were recognised in the resulting sensory space, one running from melting to thick and another one running from rough to creamy-soft. The first dimension was strongly associated with starch and carrageenan concentrations and the second one, with fat content. Most high fat custards appeared at the creamy side of the sensory space while the low-fat custards were at the rough side. Lethuaut et al (2003) observed clear differences in sweetness and in texture among dairy dessert system models with different types of carrageenan. The sample with λ-carrageenan was perceived as sweeter and with more unctuous and smooth texture than the samples with κ- and ι-carrageenan. More recently, these authors (Lethuaut, Brossard, Meynier, Rousseau, Llamas, Bousseau & Genot, 2005) investigated the aroma-sweetness interactions on dairy desserts

of different texture and concluded that the dessert composed of λ-carrageenan, which had the softest texture and was perceived as the sweetest, was also perceived as the most flavoured.

The objective of this work was to study the effects of the interactions between λ-carrageenan, crosslinked starch and milk fat on the rheological and sensory properties of vanilla dairy dessert model systems.

2. Materials and methods

2.1. Materials

Three levels of crosslinked waxy maize starch C*PolarTex® 06741 (Cerestar Ibérica, Spain) (2.5, 3.25 and 4 %), five levels of carrageenan (fraction enriched in lambda carrageenan) Satiagum ADC 25 (Degussa Texturant Systems, Spain) (0, 0.02, 0.06, 0.1 and 0.3%) and two types of milk (whole and skimmed) were considered in this study. Fixed amounts of sucrose (8%), colorant Vegex NC 2c (CHR Hansen S.A.) (0.052%) and vanilla aroma 37548ª (Lucta S.A.) (0.016%) were used. Both skim milk (0.1% fat) and whole milk (3.12% fat) were prepared 24 h in advance by dissolving 12% (w/w) of the corresponding milk powders (Central Lechera Asturiana, Asturias, Spain) in deionised water.

2.2. Viscosity profile during thermomechanical process

A Rapid Visco-Analyser (RVA) instrument (Newport Scientific, Warriewood, Australia) was utilized to prepare the samples and to follow the apparent viscosity profile of the samples as a function of temperature and time. The amounts of ingredients required to make up 25 g of sample were placed inside the aluminium canister. RVA Custard Powder Pasting Method (Method 20, version 5) (Newport Scientific, 1998) was applied as follows:

Automatic stirring action was set at 960 rpm for 10 s and then slowed to 160 rpm. The temperature of the sample was equilibrated at 50°C for 1 min, heated to 95°C for 3 min 42 s, held at 95 C for 5 min, cooled to 30ºC over 5 min and 48 s, and then held at 30ºC for 4 min 30 s. Viscosity and temperature data were recorded over time; data gathering and analysis were performed using the Thermocline for Windows software, provided by the instrument's manufacturer. Each analysis was done in duplicate.

2.3. Rheological measurements

After the thermo-mechanical or preparation process, the samples were kept at 4-5 ºC for 24 hours. Measurements were carried out in a controlled stress rheometer RS1 (Thermo Haake, Karlsruhe, Germany), using a parallel plates geometry of 6 cm diameter and 1 mm gap, monitored by a RheoWin software package (version 2.93, Haake). A temperature of 5 ±1ºC, selected as representative of the usual consumption temperature of dairy desserts, was kept during measurements with the Phoenix P1 Circulator device (Thermo Haake). Samples were allowed to rest for 15 minutes before measurement and a fresh sample was loaded for each measurement.

In order to determine the linear viscoelastic region, stress sweeps were run at 1 Hz. The frequency sweeps were performed over the range f = 0.01-10 Hz and the values of the storage modulus (G'), the loss modulus (G''), the loss tangent angle (tan δ) and the complex viscosity (η*), as a function of frequency, were calculated using the Rheowin Pro software (version 2.93, Haake).

2.4. Sensory analysis

The effect of λ-carrageenan concentration on the sensory properties of both the skim milk and the whole milk dairy desserts were studied on samples containing 3.25 % starch. Samples for sensory analysis were prepared in batches of 800g. All ingredients were weighted in a flask and mixed under magnetic stirring during 10min. The flask was placed in a water bath at 97 ± 1ºC and stirred constantly with a propeller stirrer. After 15 min the product temperature reached 85 ± 1ºC and heating was continued at this temperature for 10 min. After the heating process the evaporated water was replaced gravimetrically. The sample was cooled in a water bath at 20ºC until it reached temperatures of about 40ºC and then the aroma was added. The sample was homogenised, transferred to a closed flask and stored in refrigeration (4 ± 1ºC) for 48 h.

Differences in thickness and creaminess and in the intensity of sweetness and vanilla flavour among five samples, varying in their λ-carrageenan concentration (0, 0.02, 0.06, 0.1 and 0.3%), were analysed using ranking tests (ISO,1988a). The study was carried out by a group of 46 assessors, with previous experience on sensory analysis of dairy products, and selected according to their taste sensitivity and their capacity to detect differences in intensities of the above cited attributes (ISO, 1993). Two groups of samples, one composed of whole milk samples and the other one composed of skim milk samples were evaluated by each assessor in two different sessions. Samples (30 ml) were presented in white plastic cups coded with three digits random numbers. Mineral water was provided for mouth-rinsing. All sessions were carried out in the morning (11:00-13:00) in separate booths, in a standardised test room (ISO, 1988b). Data acquisition and analysis was performed using Compusense® *five* release 4.6 (Compusense Inc., Guelph, ON, Canada)

2.5. Statistical analysis

The effect of λ-carrageenan concentration (five levels), starch concentration (three levels) and type of milk (two levels) on the viscoelastic parameter values (G', tan δ and η*) at a frequency of 1 Hz were analysed by ANOVA including three factors with interactions. The Fisher test (α=0.05) was used to calculate the minimum significant difference. Calculations were carried out with the Statgraphics Plus 4.1 software.

Friedman Analysis of Variance was applied to the sensory data obtained in the rank tests, significance of differences between samples were determined by the Fisher test (α=0.05), modified for non-parametric data (Meilgaard, Civille & Carr, 1999) using Compusense® *five* release 4.6 (Compusense Inc., Guelph, ON, Canada)

3. Results

3.1. Viscosity-temperature profiles

In all cases, the sample viscosity began to increase at 65-70ºC (pasting temperature), increased smoothly during the heating period at 95ºC, continued to increase during cooling and the profile finalised with a plateau or a slight descending region. The viscosity-temperature profiles of samples showed quantitative differences as a function of the sample formulation. For samples without λ-carrageenan, the registered viscosity values increased with starch concentration due to the increase in the volumetric fraction of the starch granules in the dispersion and they were higher for whole milk samples than for skim milk samples (Figure 1). These results followed the same trend than those obtained by Matser & Steeneken (1997) and by Abu-Jdayil, Mohameed & Eassa (2004). The latter authors also observed that the

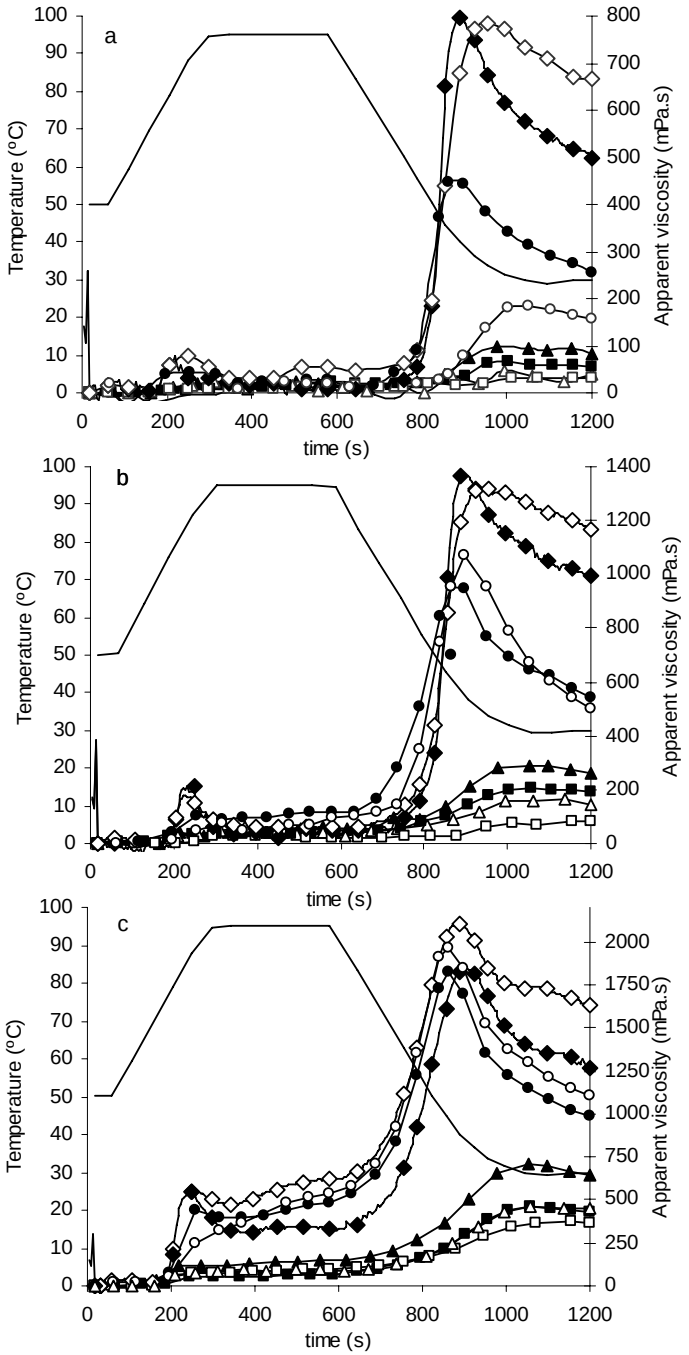

Figure 1. Viscosity profiles during thermal treatment of dairy desserts with 2.5 (a), 3.25 (b) and 4% starch concentration (c) and with different carrageenan concentrations: 0 (□), 0.02 (△), 0.1 (○) and 0.3% (◇). Whole milk samples (filled symbols) and skim milk samples (empty symbols). Temperature profile (—).

apparent viscosity of 6% wheat starch pastes at 2.2 s^{-1} increased by 5% using low fat (1.5 %) milk and by 15% using high fat (3 %) milk, compared with using skim milk (0.2% fat), and concluded that besides the effect of milk on the increase in rigidity of the starch granules, the three-dimensional fat polymers contributed to the increase in apparent viscosity of starch milk pastes. Some changes in the viscosity profile were observed with the addition of λ-carrageenan, especially in the cooling period. The addition of 0.02% λ-carrageenan resulted only in an increment of the registered viscosity values. For higher λ-carrageenan concentrations (≥0.06%), in addition to this effect, a pronounced peak during cooling was observed and the apparent viscosity reached the maximum value at higher temperatures (35-45ºC) than for the samples without λ-carrageenan (30ºC). The viscosity values registered at the end of cooling period (η_{EC}) (Figure 2), obtained from the viscosity profiles, were compared.

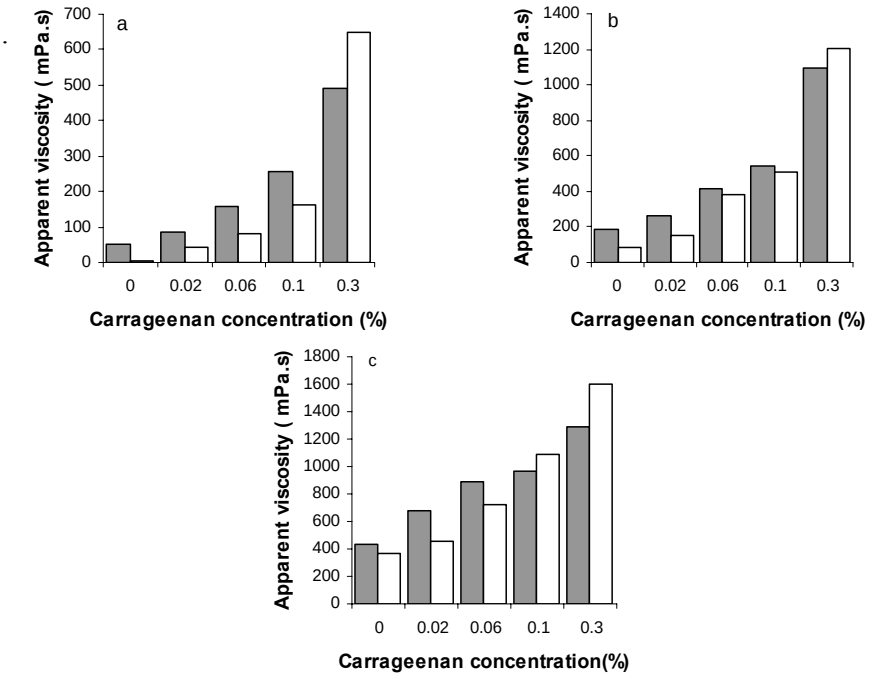

Figure 2. Apparent viscosity values at the end of the cooling time for samples with 2.5 (a), 3.25 (b) and 4% starch concentration (c). Whole milk samples (▭) and skim milk samples (▭).

The η_{EC} values increased with both λ-carrageenan concentration and starch concentration. The effect of milk fat content on η_{EC} values depended mainly on the λ-carrageenan concentration but it also varied with starch concentration, resulting in very interesting interactions: At λ-carrageenan concentration ≤ 0.06%, skim milk samples showed lower η_{EC} values than whole milk samples. At an intermediate λ-carrageenan concentration (0.1%), the effect of milk fat content depended on the starch concentration, the η_{EC} values being lower for skim milk samples at the lower starch concentrations and higher at the highest starch concentration. At the highest λ-carrageenan concentration (0.3%), they were higher for skim milk samples than for whole milk samples, at all starch concentrations.

3.2. Viscoelastic properties

The mechanical spectra of the dairy desserts, obtained from the stress sweeps experiments, showed important differences in the viscoelastic properties depending on composition. The mechanical spectra for 2.5, 3.25 and 4% starch desserts varying in λ-carrageenan concentration and fat content are represented in figures 3, 4 and 5, respectively.

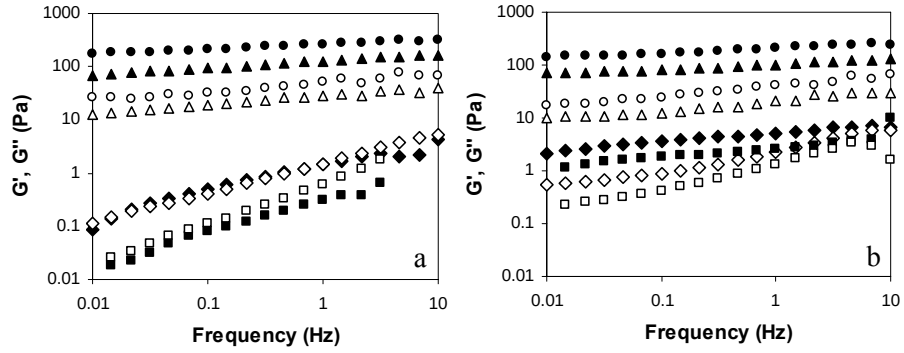

Figure 3. Mechanical spectra for dairy desserts with 2.5 % starch, skim milk (a) and whole milk (b) and different carrageenan concentrations: 0 (□), 0.02 (◇), 0.1 (△) and 0.3% (○). G' (filled symbols) and G'' (open symbols).

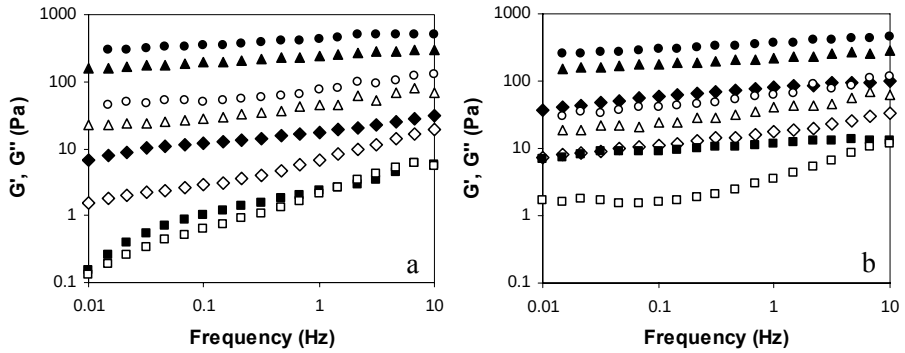

Figure 4. Mechanical spectra for dairy desserts with 3.25 % starch, skim milk (a) and whole milk (b) and different carrageenan concentrations: 0 (□), 0.02 (◇), 0.1 (△) and 0.3% (○). G' (filled symbols) and G'' (open symbols).

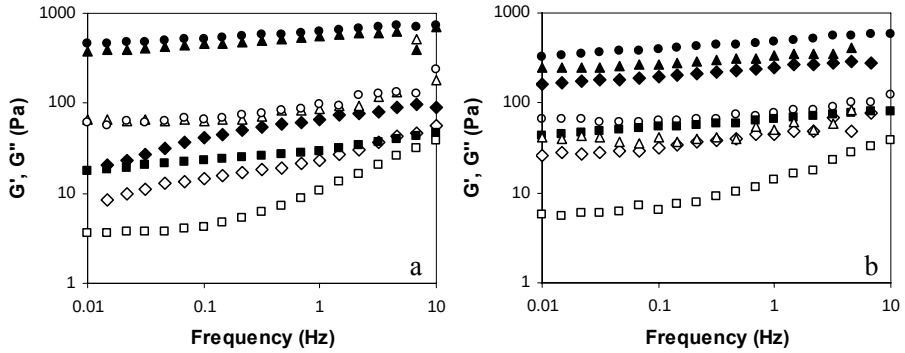

Figure 5. Mechanical spectra for dairy desserts with 4 % starch, skim milk (a) and whole milk (b) and different carrageenan concentrations: 0 (□), 0.02 (◇), 0.1 (△) and 0.3% (○). G' (filled symbols) and G'' (open symbols).

Most samples showed a clear gel-like behaviour, G´ being higher than G´´. The exceptions were found for the 2.5% and the 3.25% starch samples with skim milk and without λ-carrageenan and for the 2.5% starch sample with skim milk and with 0.02 % λ-carrageenan. They showed moduli values dependent on frequency, G'' values being higher or of the same magnitude than G' ones, indicating a more fluid-like behaviour. Addition of λ-carrageenan produced a remarkable increase in the viscoelastic functions G' and G'' and reduced the dependence on frequency of G''. These results are in agreement with the observations made by Syrbe, Bauer & Klostermeyer

(1998) about the influence of the volume fraction of dispersed particles in the effect of carrageenan concentration on the structure of dairy systems. For systems with a low volume fraction of dispersed particles (2.5% starch concentration), at low carrageenan concentration (i.e. 0.02%), where most of the polymer is adsorbed on the casein colloid particles, the product structure stays essentially unchanged. The amount of free polymer is not enough to form a gel. On the other side, for systems with a high volume fraction (3.25 and 4% starch concentration) only a low carrageenan concentration is necessary to generate a composite network.

Table 1. Storage modulus (G'), loss angle tangent (tan δ) and complex viscosity (η*) average values (n=2) at 1 Hz for dairy dessert samples.

Starch (%)	Carrageenan (%)	Milk Type[a]	G' (Pa)	tan δ	η* (Pa.s)
2.5	0	W	2.68	0.50	0.48
		S	0.29	1.89	0.10
	0.02	W	7.05	0.48	1.21
		S	1.61	0.96	0.35
	0.06	W	126.35	0.21	11.04
		S	65.89	0.24	10.78
	0.1	W	118.35	0.20	19.21
		S	136.40	0.22	22.21
	0.3	W	202.50	0.19	32.84
		S	244.50	0.19	39.64
3.25	0	W	14.56	0.45	2.42
		S	2.22	0.94	0.49
	0.02	W	65.88	0.23	10.76
		S	20.17	0.37	3.42
	0.06	W	256.00	0.18	41.39
		S	204.05	0.20	33.11
	0.1	W	248.50	0.16	40.08
		S	249.00	0.17	40.21
	0.3	W	326.75	0.17	52.73
		S	405.75	0.17	65.49
4	0	W	31.71	0.25	7.66
		S	30.94	0.36	5.23
	0.2	W	249.75	0.18	40.42
		S	94.13	0.29	15.60
	0.06	W	367.70	0.16	50.26
		S	231.30	0.18	37.43
	0.1	W	335.70	0.16	54.08
		S	524.45	0.16	84.59
	0.3	W	473.50	0.16	76.27
		S	616.75	0.16	99.32

[a] W, whole milk and S, skim milk

For comparison purposes, G', tan δ and η∗ values at a frequency of 1 Hz were considered (Table 1). An analysis of variance of three factors (λ-carrageenan concentration, starch concentration and type of milk) with interactions applied to the values of these viscoelastic parameters showed that the ternary interaction was significant for all of them (Table 2), indicating that the three considered factors contributed to the viscoelastic properties of the studied dispersions.

Table 2. Effects of type of milk, starch concentration and carrageenan concentration on values of storage modulus (G'), loss angle tangent (tan δ) and complex viscosity (η∗) at 1Hz. F and p values.

	G'		tan δ		η∗	
	F	p	F	p	F	p
Main effects						
Milk Type	0	0.9945	179.96	0.0000	1.45	0.2374
Starch Concentration	727.19	0.0000	160.48	0.0000	413.74	0.0000
Carrageenan Concentration	894.70	0.0000	240.22	0.0000	494.11	0.0000
Binary Interactions						
Milk Type x Starch Concentration	0.87	0.4284	51.48	0.0000	1.30	0.2869
Milk Type x Carrag. Concentration	62.39	0.0000	82.26	0.0000	27.65	0.0000
Starch Concentration x Carrag Concentration	51.39	0.0000	51.38	0.0000	29.35	0.0000
Ternary eractions						
Milk Type x Starch Concentration x Carrageenan Concentration	18.42	0.0000	27.48	0.0000	9.80	0.0000

The effect of carrageenan concentration on G' values was different depending on the starch concentration (Figure 6a). For example, the addition of 0.02% λ-carrageenan implied a significant increase on G' values only in the case of the 4% starch sample. The values of tan δ decreased when λ-carrageenan concentration varied from 0 to 0.06%, this effect being lower for the 4% starch concentration (Figure 6b). At ≥ 0.06% λ-carrageenan concentration, they did not vary neither with carrageenan concentration nor

with the starch concentration. These results indicated that for samples containing from 0.06 to 0.3% carrageenan, variations in starch concentration and in λ-carrageenan concentration modified the G' values but they did not modified the relative elastic contribution to the samples viscoelasticity.

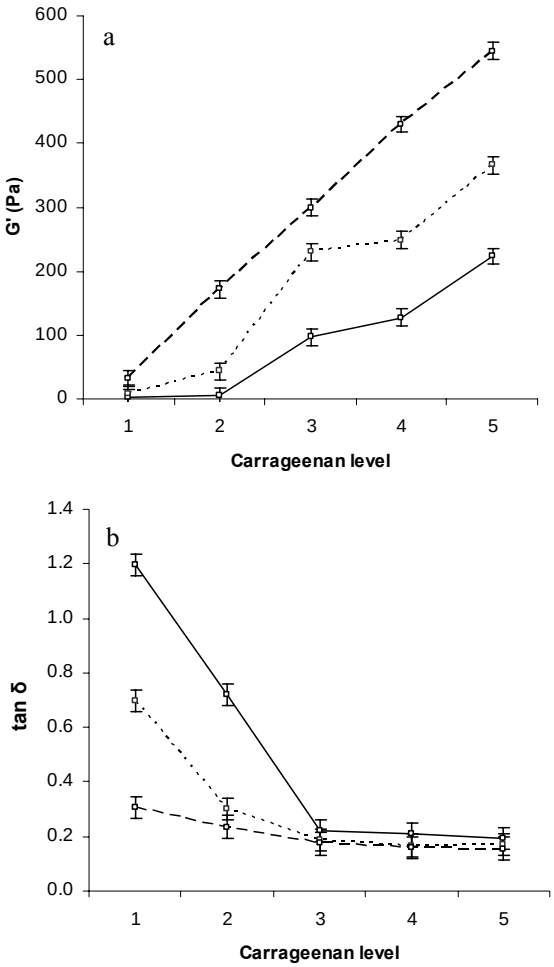

Figure 6. Variation of G'(a) and tan δ values (b) with carrageenan level. Levels 1 to 5 correspond to concentrations 0, 0.02, 0.06, 0.1 and 0.3%, respectively. Effect of starch concentration: 2.5 (—), 3.25 (·····) and 4% (-- --).

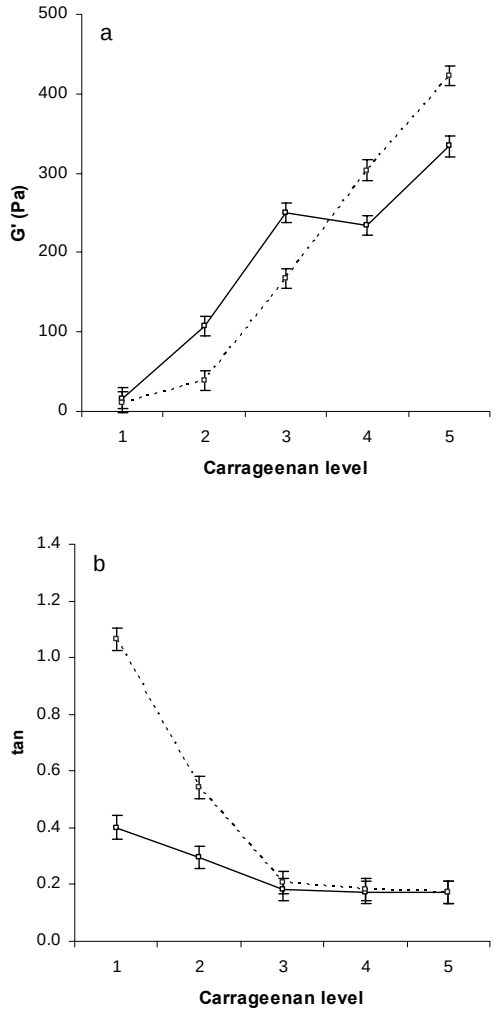

Figure 7. Variation of G'(a) and tan δ values (b) with carrageenan level. Levels 1 to 5 correspond to concentrations 0, 0.02, 0.06, 0.1 and 0.3%, respectively. Effect of milk type: Whole milk (—) and skim milk (·····).

The effect of milk fat content also depended on λ-carrageenan concentration. For λ-carrageenan concentrations lower than 0.1%, the higher fat content resulted in an increase of the G' values and for the 0.1 and 0.3% λ-carrageenan concentrations the increase in fat content resulted in a decrease of G' values (Figure7a). Values of tan δ were higher for skim milk samples

than for whole milk samples only for λ-carrageenan levels lower than 0.06% (Figure 7b). Here again, for higher λ-carrageenan concentrations, tan δ did not vary with milk fat content.

3.3. Sensory Evaluation

Analysis of the results obtained from the separate ranking tests, carried out on whole milk samples and on skim milk samples, showed significant differences (α=0.05) in thickness, in creaminess, in vanilla flavour and in sweetness intensity of samples. Friedman F values were in all cases higher than the theoretical F value (9.49 for α=0.05).

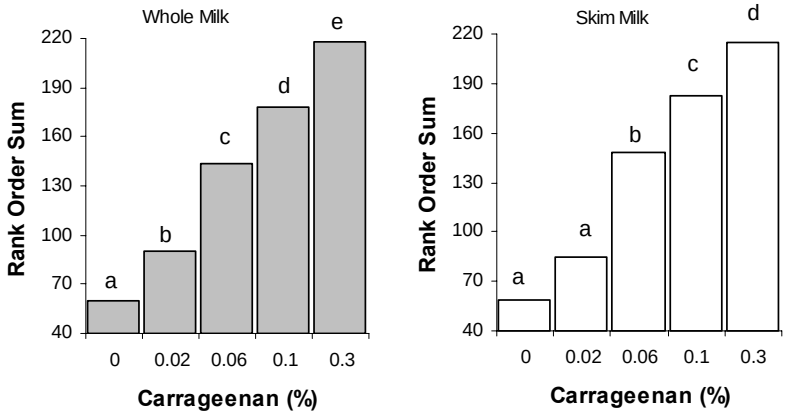

Figure 8. Sensory evaluation of thickness for dairy dessert samples with different carrageenan concentration. Different letters on top of bars mean significant differences (α=0.05).

As can be expected, the perceived thickness increased with λ-carrageenan concentration (Figure 8). The differences in thickness of the whole milk samples with different λ-carrageenan concentrations were all significant. For skim milk samples, thickness of the 0.02% λ-carrageenan sample was not significantly different from that of the sample without carrageenan. Addition

of λ-carrageenan at concentrations up to 0.06% increased creaminess for both whole milk and skim milk samples. Higher concentrations of λ-carrageenan lowered creamy sensation in whole milk samples and did not change it in skim milk samples (Figure 9). In dairy desserts, creaminess is an important attribute since it is highly correlated with consumer acceptance (Elmore, Heymann, Johnson & Hewett 1999). It has been considered that creaminess can be predicted based on two other texture attributes: thickness and smoothness (Kokini & Cussler, 1987). In our study, however, there was not a clear relation between perceived variations in thickness and in creaminess when λ-carrageenan concentration was higher than 0.06%, these results being more in accordance with those of de Wijk et al, (2003) and of Weenen, Jelema &de Wijk (2005). They observed that in custard desserts creaminess is a multi-modal attribute, that can be affected not only by texture attributes (thick, smooth, fatty, rough, grainy) but also by some taste/flavour attributes.Significant changes in vanilla flavour intensity among samples were detected for both whole milk and skim milk samples (Figure 10).

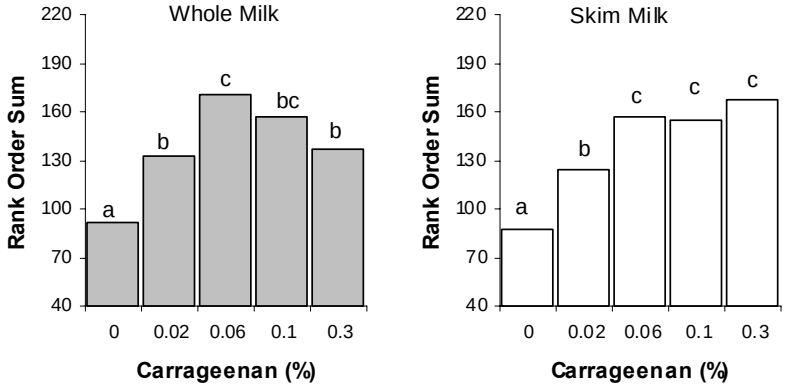

Figure 9. Sensory evaluation of creaminess for dairy dessert samples with different carrageenan concentration. Different letters on top of bars mean significant differences (α=0.05).

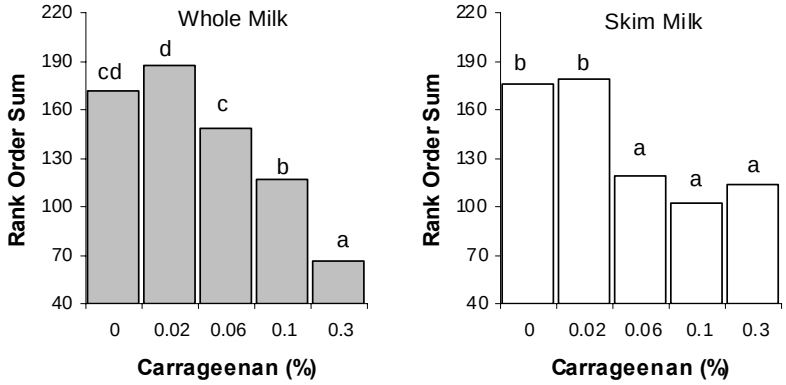

Figure 10. Sensory evaluation of vanilla flavour intensity for dairy dessert samples with different carrageenan concentration. Different letters on top of bars mean significant differences (α=0.05).

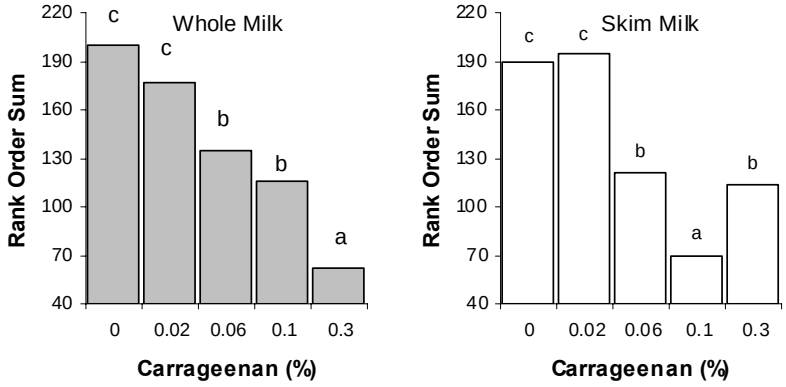

Figure 11. Sensory evaluation of sweetness intensity for dairy dessert samples with different carrageenan concentration. Different letters on top of bars mean significant differences (α=0.05).

For either group of samples, there were not significant differences in the vanilla flavour intensity perceived between the sample with 0.02% λ-carrageenan and that without λ-carrageenan. While for whole milk samples, the intensity of vanilla flavour decreased as λ-carrageenan concentration

increased (Figure 10a), for skim milk samples, those with higher λ-carrageenan concentrations (0.06 to 0.3%) were perceived as with less flavour intensity than samples with less carrageenan, but with no significant differences among them. A similar trend was observed in the variation of sweetness perceived on dairy desserts when λ-carrageenan concentration increased (Figure 11), confirming that weak gels had stronger flavour and sweetness. It is also possible that the lower intensity of vanilla flavour perceived in thicker samples may have an effect on the decrease of creaminess perceived in these samples. Weenen et al. (2005) observed that creaminess of vanilla custard desserts decreased when samples were evaluated using noseclips, indicating the positive contribution of certain flavours to creamy perception.

These results indicated that interactions among ingredients not only influenced the rheological characteristics of semisolids dairy desserts, but they may also affect their texture and flavour significantly.

Acknowledgements

To MEC of Spain for financial support (Project AGL 2003-0052) and for the fellowship awarded to author Tárrega and to the Generalitat Valenciana (through support to Group 03/147). To CHR Hansen S.A., Lucta S.A., Degussa Texturant Systems and Central Lechera Asturiana for providing free samples of the ingredients. To Dr. Luis Durán for his invaluable contribution.

References

Abu- Jdayil, B., Mohameed, H. & Eassa, A. (2004). Rheology of wheat starch-milk-sugar systems: effect of starch concentration, sugar type and concentration, and milk fat content. *Journal of Food Engineering*, 64, 207-212.

Batista, P., Nunes, M. C. & Sousa, I. (2002). Physical characterisation of commercial dairy desserts. In F.J.Martínez Boza, A. Guerrero, P.Partal, J.M. Franco & J. Muñoz., *Progress in Rheology Theory and Applications* (pp. 449-452). Sevilla: Publicaciones Digitales S.A.

De Vries, J. (2002). Interaction of carrageenan with other ingredients in dairy dessert gels. In P.A. Williams and G.O. Philips, *Gums and stabilisers for the food industry 11*. Royal Society of Chemistry, Cambridge, UK, 201-210.

De Wijk, R. A., van Gemert, L. J., Terpstra, M. E. J., & Wilkinson, C. L.(2003). Texture of semi-solids; sensory and instrumental measuraments on vanilla custard desserts. *Food Quality and Preference*, 14, 305-307

Depypere, F., Verbeken, D., Thas, O. & Dewettinck, K. (2003). Mixture design approach on the dynamic rheological and uniaxial compression behaviour of milk desserts. *Food Hydrocolloids*, 17, 311-320.

Elmore, J.R., Heymann, H., Johnson, J. & Hewett, J.E. (1999). Preference Mapping:relating acceptance of creaminess to a descriptive sensory map of a semi-solid. *Food Quality and Preference*, 10, 465-475

ISO (1988a). Sensory analysis. General guidance for design of test rooms. Standard no. 8589. Geneva, Switzerland

ISO (1988b). Sensory analysis. Methodology. Ranking. Standard no. 8587. Geneva, Switzerland

ISO (1993). Sensory analysis. General guidance for the selection, training and monitoring of assessors. Part 1: Selected assessors. Standard no. 8586-1. Geneva, Switzerland

Kokini, J.L., & Cussler, E.L (1987). The Psychophysics of Fluid Food Texture. In *Food Texture: instrumental and sensory methods*, H.R. Moskowitz, ed., Marcel Dekker, Inc., 97-127.

Langendorff V., Cuvelier G., Michon C., Launay B., Parker A. & De Kruif C.G. (2000). Effects of carrageenan type on the behaviour of carrageenan/milk mixtures, *Food Hydrocolloids* 14, 273–280.

Langendorff, V., Cuvelier, G., Launay, B., Michon, C., Parker, A. & De Kruif, C.G. (1999). Casein micelle/iota carrageenan interactions in milk: influence of temperature. *Food Hydrocolloids*, 13, 211-218

Lethuaut, L., Brossard, C., Meynier A.,Rousseau, F., Llamas G., Bousseau, B. & Genot. C. (2005). Sweetness and aroma perceptions in dairy desserts varying in sucrose and aroma levels and in textural agent. *International Dairy Journal*, 15, 485-493

Lethuaut, L., Brossard, C., Rousseau, F., Bousseau, B. & Genot. C. (2003). Sweetness-texture interactions in model dairy desserts: effect of sucrose concentration and the carrageenan type. *International Dairy Journal*, 13, 631-641.

Matser, A. M. & Steeneken, P. A. M. (1997). Rheological properties of highly cross-linked waxy maize starch in aqueous suspensions of skim milk components. Effects of the concentration of starch and skim milk components. *Carbohydrate Polymers*, 32, 297-305.

Meilgaard, M., Civille, G.V. & Carr, B.T. (1999). *SensoryEvaluation Techniques*, 3rd ed. CRCPress, Inc., Boca Raton (FL), USA

Michon, C., Chapuis, C., Langendorff, V., Boulenguer, P. & Cuvelier, G., (2005). Structure evolution of carrageenan/milk gels: effect of shearing, carrageenan concentration and nu fraction on rheological behavior. *Food Hydrocolloids*, 19, 541-547

Nadison, J. & Doreau, A. (1992). Carrageenan/starch interaction in cream desserts. In *Gums and Stabilisers for the Food Industry 6*, ed G.O. Phillips, P.A. Williams & D.J. Wedlock, Oxford University Press Ltd., 1992, 287-295.

Nunes, MC., Batista, P., Raymundo, A., Alves, M.M. & Sousa, I. (2003). Vegetable proteins and milk puddings. *Colloids and Surface B: Biointerfaces*, 31, 21-29

Shchipunov Y.A. & Chesnokov A.V (2003). Carrageenan gels in skim milk: Formation and rheological properties. *Colloid Journal* 65, 105-113

Spagnuolo, P.A., Dalgleish, D.G., Goff, H.D. & Morris, E.R. (2005). Kappa-carrageenan interactions in systems containing casein micelles and polysaccharide stabilizers. *Food hydrocolloids*, 19, 371-377

Syrbe, A., Bauer, W.J., & Klostermeyer, H. (1998) Polymer Science concepts in dairy systems- An overview of milk protein and food hydrocolloid interaction. *International Dairy Journal,* 8, 179-193

Tárrega, A., Durán, L. & Costell E. (2004). Flow behaviour of semisolid dairy desserts. Effect of temperature. *International Dairy Journal* 14, 345-353.

Tárrega, A., Durán, L. & Costell E. (2005a). Rheological characterization of semisolid dairy desserts. Effect of temperature. *Food Hydrocolloids* 19, 133-139.

Velez-Ruiz, J.F., González-Tomás, L. & Costell E. (2005) Rheology of dairy custard model systems: influence of milk fat and hydrocolloid type. *European Food Research and Technology* , 221, 342-347

Verbeken, D., Thas, O. & Dewettinck, K. (2004). Textural properties of gelled dairy desserts containing kappa-carrageenan and starch. *Food Hydrocolloids*,18, 817-823.

Weenen, H., Jellema, R.H. & de Wijk, R.A. (2005). Sensory sub-attributes of creamy mouthfeel in commercial mayonnaises, custard desserts and sauces. *Food Quality and Preference*, 16, 163-170

Wischmann, B., Norsker, M. & Adler-Nissen, J. (2002). Food product models developed to evaluate starch as food ingredient. *Nahrung/ Food*, 46, 167-173.

Yang, H., Irudayaraj, J., Otgonchimeg, S.& Walsh, M. (2004) Rheological study of starch and dairy ingredient-based food systems. *Food Chemistry*, 86, 571-578

EFFECT OF INULIN ADDITION ON RHEOLOGICAL AND SENSORY PROPERTIES OF FAT FREE STARCH BASED DAIRY DESSERTS

A. Tárrega & E. Costell*

Physical and Sensory Properties Laboratory. Instituto de Agroquímica y Tecnología de Alimentos. CSIC. P.O. Box 73. 46100 Burjassot (Valencia). Spain.

Abstract

The effect of inulin addition on the rheological and sensory properties of fat free dairy desserts containing different starch concentrations (2.5, 3.25 and 4%) was compared with the properties of full fat milk samples. All samples showed a thixotropic and shear-thinning flow behaviour. Hysteresis loops of inulin-skimmed milk samples were similar to those of whole milk samples without inulin. Skimmed milk samples showed lower consistency and lower shear-thinning than either whole milk or inulin-skimmed milk samples. Inulin addition increased both storage modulus and complex viscosity values and decreased loss angle tangent value, except in the 4% starch sample. Adding inulin to fat-free dairy model desserts increased sweetness, thickness and creaminess. At low starch concentrations, inulin-skimmed milk desserts were perceived as sweeter, with more vanilla flavour and with the same thickness as whole milk desserts but at 4% starch, the latter were thicker and creamier.

Keywords: Inulin, Dairy dessert, Fat content, Flow behaviour, Thickness, Creaminess

**Corresponding author. Tel.:+34-96-3900022; Fax: +34-96-3636301.
E-mail adress: ecostell@iata.csic.es (E.Costell).

1. Introduction

Inulin is a linear non-digestible polysaccharide of β-(2-1) linked fructose residues with a terminal glucose residue unit. It possesses the nutritional aspects of dietary fiber (Flamm, Glinsmann, Kritchevsky, Prosky & Roberfroid, 2001), stimulates the selective growth of beneficial bifido bacteria (Roberfroid, Van Loo & Gibson, 1998), increases the absorption of calcium by the body and reduces the triglyceride content of the serum and in the liver (Kaur & Gupta, 2002). Apart from its nutritional benefits, inulin is used as an ingredient in the formulation of novel foods for technological reasons. It is used for fat or sugar replacement, as a low caloric bulking agent and as a texturising agent (Tungland & Meyer, 2002). Its properties as fat mimetic have been attributed to its ability to bind water molecules and form a particle gel network (Frank, 1987). Zimeri and Kokini (2002) studied the thermal properties of inulin, and pointed out that its fat-mimetic properties might also be a consequence of its low relative crystallinity. The rheological behaviour of inulin and inulin-hydrocolloid mixtures in water were characterised by Bishay (1998), who found a synergistic effect between inulin and calcium alginate and a negative interaction between inulin and starch. More recently, Zimery and Kokini (2003), working on inulin-waxy maize starch systems, found that a change in the rheological behaviour was produced when the sample structure changed from a starch-continuous system, with inulin as the disperse phase, to an inulin-continuous system, with starch as the dispersed phase.

Starch-based dairy desserts are widely consumed in Europe (“Natillas” in Spain, “Vanilla vla” in The Netherlands or “Crème dessert” in France). Their nutritional and sensory characteristics favour their consumption by several groups of consumers, such as children or elderly people. Basically, they are formulated with milk, thickeners (starch and hydrocolloids), sucrose, aroma and colorants. In general, this type of product shows time dependent and

shear thinning flow behaviour, and viscoelastic properties typical of weak gels. Noticeable differences in rheological behaviour have been found in commercial samples (Batista, Nunes & Sousa, 2002; Tárrega, Durán & Costell, 2004 and 2005) and in model systems with different compositions (Wischman, Norsker and Alder Nissen, 2002; Lethuaut, Brossard, Rouseau, Bousseau & Genot, 2003; Velez- Ruíz, González-Tomás & Costell, 2005). De Wijk, van Gemert, Terpstra and Wilkinson (2003), using a trained panel, developed a set of sensory attributes for describing flavour, odour, mouthfeel and after feel of commercial vanilla custard desserts. Two main sensory dimensions were recognised in the resulting sensory space, one running from melting to thick and another one running from rough to creamy-soft. Most high fat custards appeared at the creamy side and low-fat custard at the rough side, suggesting that these attributes are related to product fat content.

Several studies dealing with the effect of inulin addition to dairy products can be found in the literature. Dello Staffolo, Bertola, Martino and Bevilacqua, (2004) found that yoghurt fortified with 1.3 % inulin showed no differences in viscosity and in acceptability compared with a control yoghurt. In reduced fat ice cream, the addition of inulin resulted in an increase in the viscosity values (El-Nagar, Gloves, Tudorica, Kuri & Brennan, 2002), a decrease in the freezing point (Schaller-Polovny & Smith, 2001) and an improvement in the sensory properties (Schaller-Povolny & Smith, 1999). El-Nagar et al., (2002) found that the sensory texture profiles of low fat yog-ice cream with inulin were similar to the profile of the high fat reference and different from that of the low fat control sample. In another type of dairy product, low-fat fresh Kashar cheese, the addition of 5 % inulin also improved their textural, melting and sensory properties (Koka & Metin, 2004). There is no information available about the influence of inulin addition on the characteristics of starch-based dairy desserts.

The aim of this work was to study the effect of inulin addition on the rheological and sensory properties of fat-free dairy dessert model systems containing different starch concentrations and to compare them with their full fat counterparts.

2. Materials and methods

2.1. Materials

A hydroxypropylated waxy maize di-starch phosphate (C* PolarTex 06741)(Cerestar Ibérica, Spain), inulin of long average chain length (≥ 23 monomers) (Frutafit TEX!, Sensus) (Brenntag Química, Spain), colorant Vegex NC 2c (CHR Hansen S.A.), vanilla aroma 37548A (Lucta S.A.), skimmed and whole milk powders (Central Lechera Asturiana, Spain) and commercial sucrose were used. Both skimmed milk (0.1% fat) and whole milk (3.12% fat) were prepared 24h in advance by dissolving 12% (w/w) milk powder in deionised water and stored in a refrigerator (4±1ºC).

Three sets of dairy desserts were prepared: skimmed milk desserts (80% skimmed milk), skimmed milk desserts with inulin (80% skimmed milk and 6% inulin) and whole milk desserts (80% whole milk). In each set, three samples with different concentrations of starch (2.5, 3.25 and 4%, w/w) were prepared. All samples also included fixed amounts of sucrose (8%, w/w), colorant (0.052%, w/w) and vanilla aroma (0.016, w/w) and deionised water was added up to 100%.

2.2. Viscosity profile during the thermomechanical process

A Rapid Visco-Analyser (RVA) instrument (Newport Scientific, Warriewood, Australia) was utilized to prepare the samples and follow the apparent viscosity profile of the samples as a function of temperature and time. The ingredient amounts required to prepare 25 g of sample were placed

inside the aluminium canister fitted with a plastic stirring paddle. RVA Custard Powder Pasting Method (Method 20, version 5) (Newport Scientific, 1998) was applied as follows: automatic stirring action was set at 960 rpm for 10 s and then slowed to 160 rpm. The temperature of the sample was equilibrated at 50 °C for 1 min, heated to 95 °C for 3 min 42 s, held at 95 °C for 5 min, cooled to 30ºC over 5 min 48 s, and then held at 30ºC for 4 min 30 s. Viscosity and temperature were recorded over time; data gathering and analysis were performed using Thermocline for Windows software, provided by the instrument manufacturer. Each analysis was done in duplicate.

2.3. Rheological measurements

After the thermo-mechanical preparation process, the samples were kept at 4-5 ºC for 24 hours. Then both the flow and the viscoelastic behaviour of each sample were measured in duplicate.

Measurements were carried out in a controlled stress rheometer RS1 (Thermo Haake, Karlsruhe, Germany), using parallel plates geometry of 6 cm diameter and 1mm gap, monitored by a RheoWin software package (version 2.93, Haake). A temperature of 5 ±1 ºC, selected as representative of the usual consumption temperature of dairy desserts, was maintained during measurements by means of a Phoenix P1 Circulator device (Thermo Haake). Samples were allowed to rest for 15 minutes before measurement and a fresh sample was loaded for each measurement.

Flow behaviour. Sample flow was measured by recording shear stress values when shearing the samples with a linear increasing shear rate from 1 to 200 s^{-1} for a period of 60 s and in reverse sequence for the same time. Areas under the upstream data point curve (A_{up}) and under the downstream data point curve (A_{down}) as well as the hysteresis area (A_{up} - A_{down}) were obtained

using Rheowin Pro software (version 2.93, Haake). The percentage of relative hysteresis area (Dolz, González, Delegido, Hernández, & Pellicer, 2000 and Tárrega et al., 2004a) was calculated by equation (1).

$$A_r = (A_{up} - A_{down})/ A_{up} \times 100 \qquad (1)$$

Data from the ascending segment of the shear cycle were fitted to the Ostwald de Waele model (Equation 2) using Rheowin Pro software (version 2.93, Haake).

$$\sigma = K \dot{\gamma}^n \qquad (2)$$

where K ($Pa.s^n$) is the consistency index and n is the flow index. Since parameter K units depend on n values, apparent viscosity values at $1s^{-1}$ (η_1) were used to compare sample consistency.

Viscoelastic properties. In order to determine the linear viscoelastic region, stress sweeps (0.01- 100 Pa) were run at 1 Hz. The frequency sweeps were then performed at 0.03 Pa over the range f = 0.01-10 Hz and the values of the storage modulus (G'), the loss modulus (G''), the loss tangent angle (tan δ) and the complex viscosity (η^*), as a function of frequency, were calculated using the Rheowin Pro software (version 2.93, Haake).

2.4. Sensory analysis

Samples for sensory analysis were prepared in batches of 800g. All ingredients were weighed in a flask and mixed using a magnetic stirrer for 10 min. The flask was placed in a water bath at 97 ± 1ºC and stirred constantly with a propeller stirrer. After 15 min, the product temperature reached 85 ± 1ºC and heating was continued at this temperature for 10 min. After the heating process, the evaporated water was replaced gravimetrically. The sample was cooled in a water bath set at 20ºC until it reached a temperature of about 40ºC and then the aroma was added. The sample was

homogenised, transferred to a closed flask and stored in a refrigerator (4 ± 1ºC) for 48 h. The above described conditions were selected to get samples with the same rheological properties that those of the RVA samples.

Differences in the intensity of sweetness and vanilla flavour and in thickness and creaminess between skimmed and whole milk dairy samples, between skimmed milk and skimmed milk-inulin samples, and between whole milk and skimmed milk-inulin samples for each starch concentration were analysed using the paired comparison test (ISO, 1983). The study was carried out by a group of 40 assessors with previous experience with sensory analysis of dairy products and selected according to their taste sensitivity and their capacity to detect differences in the intensities of the above cited attributes (ISO, 1993). Each assessor evaluated three pairs of samples per session over three sessions. In order to reduce the possible effect of the serving order, for each pair of samples an equal number of assessors received a different sample first. Samples (30 ml) were presented in white plastic cups coded with three digit random numbers. Mineral water was provided for mouth-rinsing. All sessions were carried out in the morning (11:00-13:00) in separate booths, in a standardised test room (ISO, 1988). Data acquisition and analysis was performed using Compusense® Five release 4.6 software (Compusense Inc. Guelph, ON, Canada). Tests were considered two-tailed and significant differences were established for α=0.05.

2.5. Statistical analysis

The effects of starch concentration and of the type of dessert (skimmed milk, skimmed milk–inulin, and whole milk dessert) and their interaction on the flow parameters (A_r, η_1 and n) values and on the viscoelastic parameters (G', tan δ and η*) values at 1Hz were analysed by a two way ANOVA. For each level of starch concentration, one way ANOVA was performed and the Fisher´s least significant difference (α=0.05) was calculated to determine

differences between the three types of dessert. All calculations were carried out with the Statgraphics Plus 4.1 software.

3. Results

3.1. Viscosity-temperature profiles

The viscosity-temperature profiles for all samples showed a similar pattern although clear differences were observed among them, depending on starch concentration and milk fat contents (Figure 1). In general, the viscosity began to increase at 65-70ºC (starch swelling temperature), increased smoothly during the heating period at 95ºC, continued to increase during cooling and the profile ended with a plateau or descending region. As expected, the registered apparent viscosity values were higher when the starch concentration increased, due to the increase in the volumetric fraction of the starch granules in the dispersion. For all starch concentrations, these values were higher for samples containing whole milk than for samples containing skimmed milk. These results followed the same trend as those obtained on starch-milk systems by other authors. Abu-Jdayil, Mohameed and Eassa (2004) observed that the apparent viscosity of 6% wheat starch pastes at 2.2 s^{-1} increased by 15% using high fat (3%) milk, as compared with using skimmed milk (0.2% fat), and concluded that besides the effect of milk on the increase in rigidity of the starch granules, the presence of three-dimensional fat polymers contributed to the increase in apparent viscosity of starch milk pastes. Vélez Ruiz et al (2005) also found that the milk fat content strongly influenced the apparent viscosity values registered during pasting behaviour on dairy custard model systems with different types of added hydrocolloid.

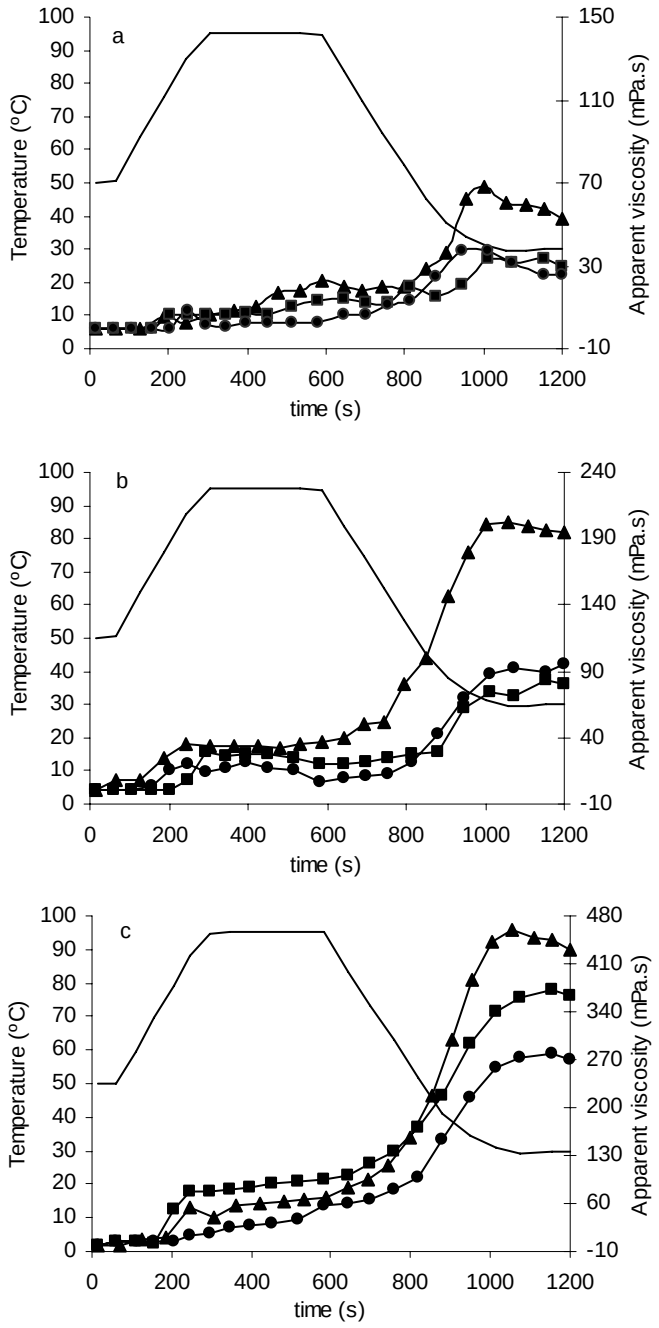

Figure 1. Viscosity profiles during thermal treatment of dairy desserts containing (a) 2.5, (b) 3.25 and (c) 4% starch. Skimmed milk desserts (■), skimmed milk-inulin desserts (●) and whole milk desserts (▲). Temperature profile (—).

The addition of inulin to skimmed milk samples did no modify the viscosity-temperature profile for samples with 2.5% and 3.25% starch concentrations (Figure 1a and 1b). For the 4% starch concentration sample, lower registered apparent viscosity values were observed when inulin was added (Figure 1c). Although there is no previous information about the rheological behaviour and the structure of milk-inulin-starch systems, the results obtained in this work can be related with the observations made by other authors in water-inulin-starch systems. Bishay (1998) detected a "negative synergy" between inulin and starch in water. The addition of 35% inulin to a dispersion of 10% starch clearly lowered the system consistency. According to this author, this fact can be due to a greater affinity of inulin over starch for water. More water was bound to shorter, faster moving inulin chains, and the result was a lower viscosity. More recently, Zimeri and Kokini (2003) studied the rheological properties of water-inulin starch systems with different total polymer concentrations at different ratios of inulin to starch, and found that for a total polymer concentration lower than 20%, in which starch, the more elastic component, embedded inulin chains, the zero shear viscosity value decreased with increasing inulin content. They concluded that inulin did not interact synergistically with starch and that, under these conditions, inulin could act as a diluent. In our samples, despite differences in composition and structure, attributable to the presence of caseins, whey proteins and other milk components and to the effect of the sucrose addition (8%), the different effect of inulin on samples with different starch concentration could be explained by the inulin and starch competing for water. In the samples with lower starch concentrations (2.5 and 3.25%), there was sufficient water in the system so that the addition of inulin did not influence the starch granule swelling process. For samples with the higher starch concentration (4%), with part of the water bound to the inulin chains, swelling of the starch granules was limited, the volume fraction of swollen particles was lower and the system viscosity decreased.

3.2. Flow behaviour

All samples exhibited time dependent and shear thinning flow behaviour (Figure 2) This type of behaviour is in accordance with previous observations on commercial samples of semi-solid dairy desserts (Tárrega et al. 2004a). The time dependent behaviour (thixotropic or antithixotropic) of water-starch pastes has been reported by several authors (Nguyen, Jensen & Kristensen, 1998, Tecante & Doublier, 1999; Tattiyakul & Rao, 2000) but less information is available about this type of behaviour in milk starch dispersions. Recently, Abu-Jdayil and Mohameed (2004) studied the time-dependent flow properties of native starch-milk-sugar pastes and observed that the degree of thixotropy increased significantly with starch concentration. Tárrega, Vélez and Costell (2005) analysed the influence of whole milk on the flow of dispersions of different cross-linking modified starches compared to aqueous dispersions at the same starch concentrations. They observed that substitution of milk by water caused an increase in the hysteresis loop area and that the samples that showed antithixotropy in water (6% maize starch concentration) showed thixotropy in milk dispersions. In this case, for each starch concentration, the magnitude and the form of the hysteresis loop of inulin-skimmed milk samples were more related to those of whole milk than to those of skimmed milk samples without inulin (Figure 2). Considering the relative thixotropic area values, the analysis of variance, showed significant effects of starch concentration ($F=13.21$, $p=0.002$) and of type of dessert ($F=55.18$, $p=0.000$) and no significant interaction between the two factors ($F_{int}=3.42$, $p=0.058$), indicating that the effect of variation of the composition on the structure responsible for flow time dependence was similar for the different starch concentrations. Analysing differences among samples with the same starch concentration, we found that for the three starch concentrations considered, the loop areas of skimmed milk samples were significantly smaller than those of inulin-skimmed milk and of whole

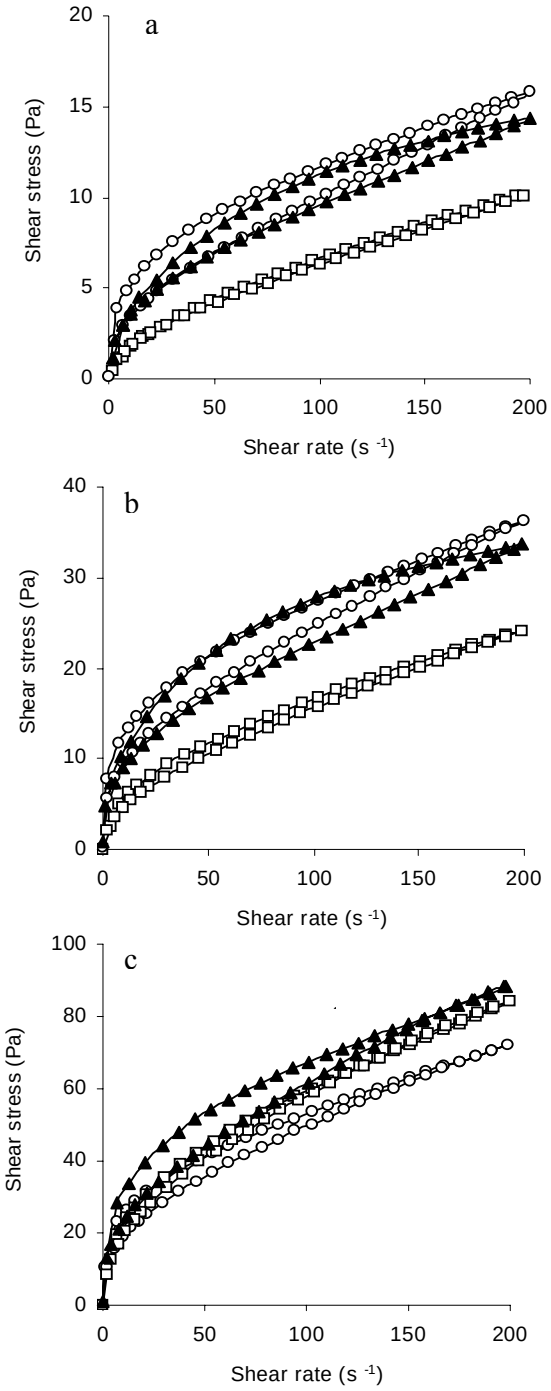

Figure 2. Flow behaviour of dairy desserts containing (a) 2.5, (b) 3.25 and (c) 4% starch. Skimmed milk desserts (□), skimmed milk-inulin desserts (○) and whole milk desserts (▲).

milk samples, and that no significant differences were detected between the latter ones (Figure 3). Assuming that a hysteresis loop area is an index of the energy needed to destroy the structure responsible for flow time dependence, the experimental data indicated that the energy needed to breakdown such structure was similar in the samples with full fat content and in the skimmed milk samples with inulin. According to Schaller-Povolny and Smith (2002), this fact can be due to the ability of inulin to bind water molecules and to the possible interaction between some milk proteins and inulin. This interaction could increase the molecular weight of the milk protein fraction, thus increasing the viscosity of the continuous phase. The effect of these modifications on the structure responsible for flow time dependence of inulin-skimmed milk samples was similar to the effect due to fat in the whole milk samples.

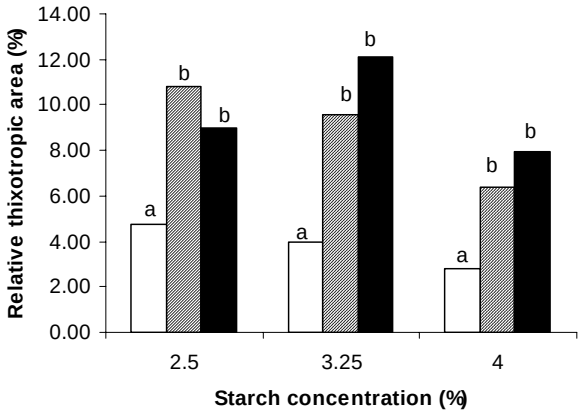

Figure 3. Relative thixotropic area values of dairy desserts at different starch concentration. Skimmed milk desserts (white bars), skimmed milk-inulin desserts (striped bars) and whole milk desserts (black bars). For each starch concentration, different letters on top of bars mean significant differences (α=0.05).

Characterisation of the flow behaviour of samples was determined from the experimental data obtained in the upward rheogram. Flow data fitted well to the Ostwald de Waele model with R^2 values between 0.9922 and 0.9994. As expected, in the three types of dessert, the consistency coefficient (K) values increased with starch concentration while the flow index (n) values decreased (Table 1). A two-way ANOVA with interaction was used to study the combined effects of the type of dessert and the starch concentration on the variations of apparent viscosity at $1s^{-1}$ (η_1) and of flow index (n). For both parameters the interaction between these factors was significant (F_{int} = 9.00, p= 0.0033 and F_{int} = 14.9, p= 0.0005 respectively) indicating that the effect of composition of the dessert sample on both parameter values was different, depending on starch concentration.

Table 1. Ostwald de Waele fit of dairy dessert flow curves. Consistency index (K) and flow index (n) values [a] [b].

Starch concentration (%)	Dessert type	K ($Pa.s^n$)	n
2.5	Fat free	0.40 ± 0.03	0.60 ± 0.03
	Fat free-inulin	1.82 ± 0.20	0.40 ± 0.01
	Full fat	1.34 ± 0.20	0.45 ± 0.02
3.25	Fat free	1.50 ± 0.09	0.52 ± 0.01
	Fat free-inulin	4.47 ± 0.8	0.37 ± 0.00
	Full fat	5.25 ± 0.21	0.35 ±0.02
4	Fat free	7.03 ± 0.37	0.46 ± 0.00
	Fat free-inulin	8.92 ± 0.86	0.39 ± 0.01
	Full fat	12.97 ± 0.06	0.36 ± 0.01

a. Average values of two measurements ± SD (α=0.05)
b. $0.9922 \leq R^2 \leq 0.9994$

For each starch level, flow of skimmed milk samples showed significantly lower apparent viscosity value at $1s^{-1}$ (Figure 4) and higher flow index value. For both parameters, no significant differences between whole milk and inulin-skimmed milk samples were found at 2.5 and 3.25% starch concentration. At 4% starch concentration, the whole milk sample showed significantly higher apparent viscosity value at $1s^{-1}$ and more shear-thinning flow than the inulin-skimmed milk sample. These results indicate that, at low starch content, inulin has a remarkable capacity to replace fat in semi solid starch-based dairy desserts.

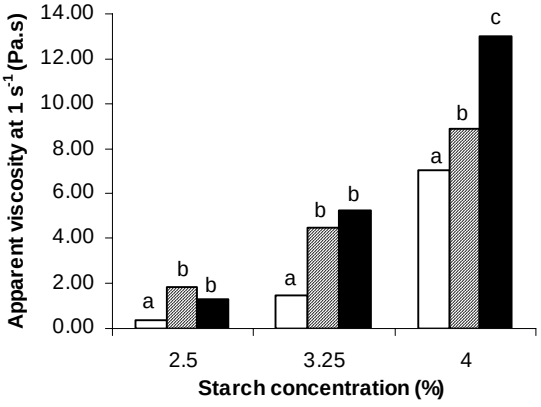

Figure 4. Apparent viscosity values at 1 s^{-1} of dairy desserts at different starch concentrations. Skimmed milk desserts (white bars), skimmed milk-inulin desserts (striped bars) and whole milk desserts (black bars). For each starch concentration, different letters on top of bars mean significant differences (α=0.05).

3.3. Viscoelastic properties

Mechanical spectra of inulin-skimmed milk samples and whole milk samples showed a response typical of weak gels with a storage modulus (G') higher than loss modulus (G''), the latter one showing higher frequency dependence (Figure 5). Skimmed milk samples without inulin, containing 2.5% starch, showed a fluid-like behaviour with values of G'' higher than G' (Figure 5a),

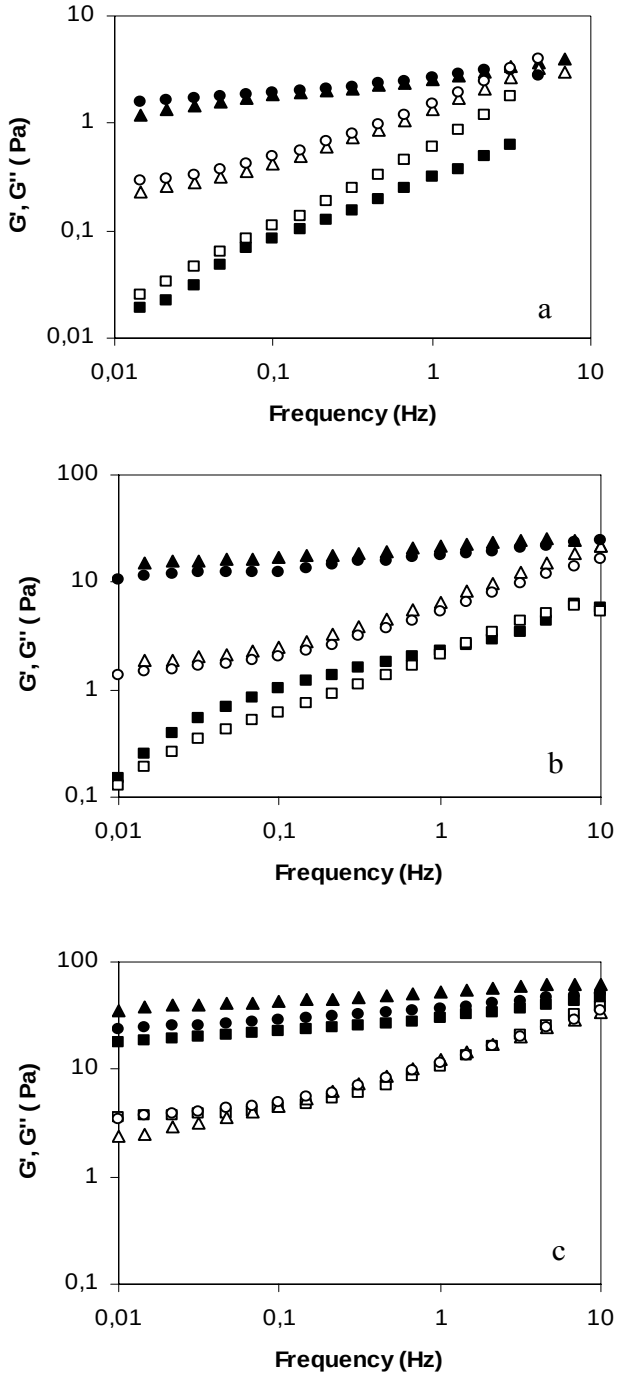

Figure 5. Mechanical spectra for dairy desserts containing (a) 2.5, (b) 3.25 and (c) 4% starch. Skimmed milk desserts (□), skimmed milk-inulin desserts (○)and whole milk desserts (△). G' (filled symbols) and G'' (open symbols).

while those with 3.25% starch showed G' values slightly higher G'' values at low frequencies but of the same magnitude at high frequencies, indicating a very weak gel structure (Figure 5b). At 4% starch concentration the mechanical spectra of the three types of dessert appeared to be similar (Figure 5c).

For comparison purposes, G', tan δ and η∗ values at a frequency of 1 Hz were considered (Table 2). Both storage modulus and complex viscosity increased and loss angle tangent decreased with starch concentration, indicating an increase in the relative elastic contribution of this ingredient to the samples viscoelasticity.

Table 2. Storage modulus (G'), loss angle tangent (tan δ) and complex viscosity (η∗) values at 1 Hz for dairy desserts.

Starch concentration (%)	Dessert type	G' (Pa)	tan δ	η∗ (Pa.s)
2.5	Fat free	0.29 [a]	1.89 [b]	0.10 [a]
	Fat free-inulin	2.89 [b]	0.54 [a]	0.52 [b]
	Full fat	2.68 [b]	0.50 [a]	0.48 [b]
3.25	Fat free	2.22 [a]	0.94 [b]	0.48 [a]
	Fat free-inulin	15.92 [b]	0.35 [a]	2.69 [b]
	Full fat	14.56 [b]	0.45 [a]	2.42 [b]
	Fat free	30.94 [a]	0.36 [c]	5.23 [a]
	Fat free-inulin	34.72 [a]	0.32 [b]	5.80 [a]
	Full fat	46.71 [b]	0.25 [a]	7.66 [b]

[1] Average values of two measurements. For each starch concentration, values with different letter superscript are significantly (α=0.05) different.

For all parameters, two way ANOVA showed a significant interaction between starch concentration and dessert type (F_{int} = 9.00, p= 0.0033, F_{int} = 43.6, p= 0.0000 and F_{int} = 8.20, p= 0.0045 for G', tan δ and η∗ at 1Hz, respectively), indicating that the effect of changing dessert composition on viscoelasticity was also different depending on the starch concentration. For samples with 2.5 and 3.25% starch, inulin added to skimmed milk dispersions showed the same effect as with fat on whole milk samples: increased both storage modulus and complex viscosity values and decreased loss angle tangent. Again the exception was found at 4% starch concentration. No significant differences were detected between G' and η∗ values for inulin-skimmed milk and skimmed milk samples and both of them showed a significantly higher tan δ value than the whole milk samples (Table 2).

3.4. Sensory Evaluation

It can be expected that the observed changes in the rheological behaviour, induced by inulin addition, may modify the samples texture and flavour perceived. According to de Wijk, et al. (2003), the two main sensory dimensions of texture of commercial vanilla custard desserts were related to thickness and to creaminess. Although it has been considered that inulin has a bland neutral taste without any off flavour or aftertaste (Frank, 2002), its effect on flavour of vanilla dairy desserts may be different to the effect of fat.

Differences in sweetness, vanilla flavour intensity, thickness and creaminess among the different model dairy desserts analysed, were evaluated by three series of paired comparison tests. First, the effect of fat content on flavour and texture was evaluated by comparing skimmed milk and whole milk samples. Secondly, the effect of inulin on these sensory attributes was

evaluated by comparing skimmed milk and inulin-skimmed milk samples and finally, perceptible differences between whole milk and inulin-skimmed milk samples were analysed. For all starch levels, whole milk model desserts were perceived as thicker and creamier than their skimmed milk counterparts. No significant differences in sweetness and in vanilla flavour intensity were detected in samples with the same starch concentration (Figure 6).

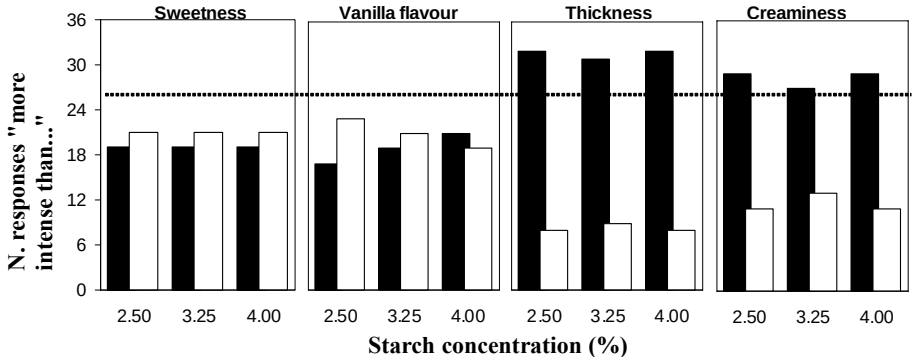

Figure 6. Sensory evaluation of the differences between skimmed milk desserts (white bars) and whole milk desserts (black bars) at different starch concentrations. The line indicates the minimum value of response for which the difference is significant (α=0.05).

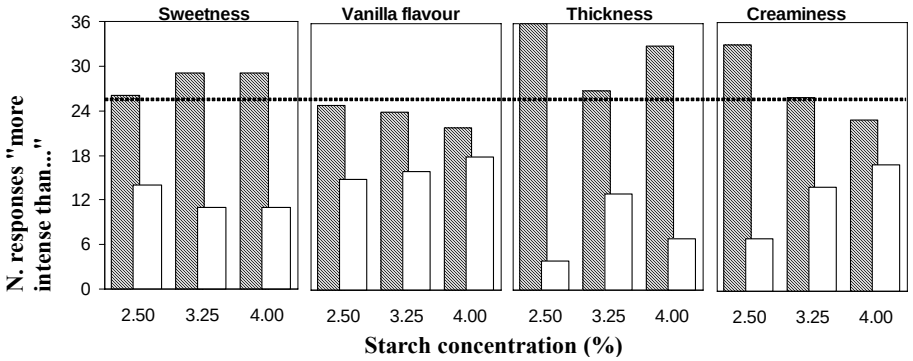

Figure 7. Sensory evaluation of the differences between skimmed milk desserts (white bars) and skimmed milk-inulin desserts (striped bars) at different starch concentrations. The line indicates the minimum value of response for which the difference is significant (α=0.05).

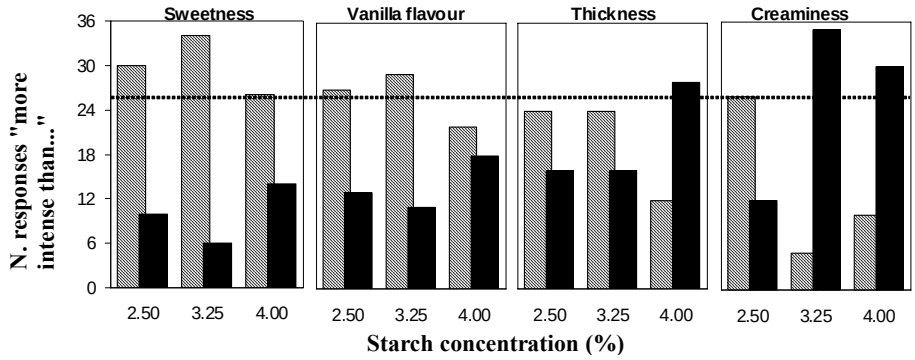

Figure 8. Sensory evaluation of the differences between skimmed milk-inulin desserts (striped bars) and whole milk desserts (black bars) at different starch concentrations. The line indicates the minimum value of response for which the difference is significant (α=0.05).

Adding inulin to fat-free dairy model desserts resulted in a significant increase in sweetness, thickness and creaminess except for samples with 4% starch concentration, which showed no difference in creaminess compared with skimmed milk sample. No significant changes in vanilla flavour intensity among samples were detected (Figure 7). The effect of fat replacement with inulin on sensory characteristics of samples was evaluated by comparing inulin fat-free and full fat desserts. In this case, the differences between samples highly depended on starch concentration (Figure 8). At 2.5 and 3.25% starch concentrations, no differences in thickness were perceived between inulin fat-free and full fat desserts but at 4% starch concentration the full fat dessert was thicker. Creaminess of inulin fat-free dessert was significantly higher than that of full fat dessert at 2.5% starch concentration. At higher starch levels, full fat desserts were perceived creamier. Except for samples with 4% starch concentration, inulin fat-free samples were perceived as sweeter and with more vanilla flavour intensity than whole milk samples.

4. Conclusions

It can be concluded that the effects of 6% inulin addition on the rheological behaviour of starch-based dairy products are clearly dependent on starch concentration, due to the competition between inulin and starch for water. The clear influence of inulin on sweet taste and on vanilla flavour intensity in skimmed milk samples with lower starch concentrations suggests a faster flavour release in these systems. These results are of interest in the formulation of low-fat starch based dairy desserts with inulin addition, but more information is needed on the combined effects of the different ingredients, in order to optimise their nutritional and sensory characteristics.

Acknowledgements

To MEC of Spain for financial support (Project AGL 2003-0052) and for the fellowship awarded to author Tárrega. To CHR Hansen S.A., Lucta S.A., Brenntag Química and Central Lechera Asturiana for providing free samples of the ingredients. To Dr. Luis Durán for his valuable contribution.

References

Abu- Jdayil, B. & Mohameed, H. & (2004). Time-dependent flow properties of starch-milk-sugar pastes. *European Food Research And Technology*, 218, 123-127.

Abu- Jdayil, B., Mohameed, H. & Eassa, A. (2004). Rheology of wheat starch-milk-sugar systems: effect of starch concentration, sugar type and concentration, and milk fat content. *Journal Of Food Engineering,* 64, 207-212.

Batista, P., Nunes, M. C. & Sousa, I. (2002). Physical characterisation of commercial dairy desserts. In F.J. Martínez Boza, A. Guerrero, P.

Partal, J.M. Franco & J. Muñoz., *Progress in Rheology Theory and Applications.* Publicaciones Digitales S.A. Sevilla, Spain, 449-452.

Bishay I. E. (1998) Rheological Characterization of Inulin. In P.A. Williams and G.O. Philips, *Gums and stabilisers for the food industry 11*. Royal Society of Chemistry, Cambridge, UK, 201-210.

De Wijk, R. A., van Gemert, L. J., Terpstra, M. E. J., & Wilkinson, C. L.(2003). Texture of semi-solids; sensory and instrumental measuraments on vanilla custard desserts. *Food Quality and Preference*, 14, 305-307

Dello Staffolo, M., Bertola, N., Martino, M. & Bevilacqua, A. (2004). Influence of dietary fiber addition on sensory and rheological properties of yogurt. *International Dairy Journal*, 14, 263-268.

Dolz, M., González, F., Delegido, J., Hernández, M. J., & Pellicer, J. (2000). A time-dependent expression for thixotropic areas. Application to aerosil 100 hydrogels. *Journal of Pharmaceutical Sciences*, 89, 790-797.

El-Nagar, G., Clowes, G., Tudorica, C.M., Kuri, V. and Brennan, C.S. (2002). Rheological quality and stability of yog-ice cream with added inulin. *International Journal of Dairy Technology*, 55, 89–93.

Flamm, W. Glinsmann, D. Kritchevsky, L. Prosky & M. Roberfroid (2001). Inulin and oligofructose as dietary fiber: a review of the evidence. *Critical Reviews in Food Science and Nutrition,* 41, 353–362.

Franck, A. (2002). Technological functionality of inulin and oligofructose. *British Journal of Nutrition*, 2, 287-291.

ISO (1983). Sensory analysis. Methodology. Paired comparison test. Standard no. 8587. Geneva, Switzerland.

ISO (1988). Sensory analysis. General guidance for design of test rooms. Standard no. 8589. Geneva, Switzerland.

ISO (1993). Sensory analysis. General guidance for the selection, training and monitoring of assessors. Part 1: Selected assessors. Standard no. 8586-1.

Kaur, N. & Gupta, A. K. (2002). Applications of inulin and oligofructose in health and nutrition. *Journal of Biosciences*, 27, 703-714.

Koca, N. & Metin, M. (2004) .Textural, melting and sensory properties of low-fat fresh kashar cheeses produced by using fat replacers. *International Dairy Journal*, 14, 365-373.

Lethuaut, L., Brossard, C., Rousseau, F., Bousseau, B. & Genot. C. (2003). Sweetness-texture interactions in model dairy desserts: effect of sucrose concentration and the carrageenan type. *International Dairy Journal*, 13, 631-641.

Nguyen, Q. D., Jensen, C. T. B., & Kristensen P. G. (1998). Experimental and modelling studies of the flow properties of maize and waxy maize starch pastes. *Chemical Engineering Journal*, 70, 165-171.

Roberfroid, M.B., Van Loo, J.A E. & Gibson, G.R. (1998). The bifidogenic nature of chicory inulin and its hydrolysis products. *Journal of Nutrition*, 128, 11-19.

Schaller-Povolny, L. A. & Smith D. E. (1999). Sensory attributes and storage life of reduced fat ice cream as related to inulin content. *Journal of Food Science*,64, 555–559.

Schaller-Povolny, L. A. & Smith D. E. (2001) .Viscosity and freezing point of a reduced fat ice cream mix as related to inulin content. *Milchwissenschaft-Milk Science International,* 56, 25-29.

Tárrega, A., Durán, L. & Costell, E. (2004). Flow behaviour of semi-solid dairy desserts. Effect of temperature. *International Dairy Journal*, 14, 345-353.

Tárrega, A., Durán, L. & Costell, E. (2005). Rheological characterization of semisolid dairy desserts. Effect of temperature. *Food Hydrocolloids*, 19, 133-139.

Tárrega, A., Vélez-Ruiz, J.F. & Costell, E. (2005) Influence of milk on the rheological behaviour of cross-linked waxy maize and tapioca starch dispersions. *Food Research International*, 38, 759-768.

Tattiyakul, J.& Rao, M. A. (2000). Rheological behavior of cross-linked waxy mayze starch dispersions during and after heating. *Carbohydrate Polymers*, 43, 215-222.

Tecante, A., & Doublier, J. L.(1999). Steady flow and viscoelastic behavior of crosslinked waxy cornstarch-k-carrageenan pastes and gels. *Carbohydrate Polymers*, 40, 221-231.

Tungland, B.C. & Meyer, D. (2002) Non digestible oligo-and polysaccharides (dietary fiber): their physiology and role in human health and food. Comprehensive reviews in food science and food safety, 1, 73-92.

Vélez-Ruiz, J.F, González-Tomás, L. & Costell, E.(2005). Rheology of dairy custard model systems: Influence of milk fat and hydrocolloid type. *European Food Research and Technology*, 221, 342-347.

Wischmann, B., Norsker, M. & Adler-Nissen, J. (2002). Food product models developed to evaluate starch as food ingredient. *Nahrung/ Food*, 46, 167-173.

Zimeri, J.E. & Kokini, J.L. (2002).The effect of moisture content on the crystallinity and glass transition temperature of inulin. *Carbohydrate Polymers*, 48, 299–304.

Zimeri, J.E. & Kokini, J.L. (2003). Rheological properties of inulin–waxy maize starch systems. *Carbohydrate Polymers* 52, 67–85.

RESUMEN Y DISCUSIÓN DE LOS RESULTADOS

1. Propiedades físicas y sensoriales de muestras comerciales de natillas de vainilla

En esta primera etapa de la tesis, se planteó la necesidad de estudiar y caracterizar instrumental y sensorialmente la textura y el color de las muestras comerciales de natillas españolas. Se realizaron unos ensayos previos y se seleccionaron siete muestras de distinta marca, que representaban la variabilidad de este producto en el mercado.

Las propiedades reológicas de las natillas de vainilla comerciales se estudiaron a dos temperaturas representativas de las habituales de consumo (5 y 25ºC), utilizando diferentes tipos de ensayos reológicos. Todas las muestras presentaron un comportamiento de flujo dependiente del tiempo, con una cierta resistencia inicial a fluir y pseudoplástico. La dependencia del tiempo del flujo de las muestras se evaluó cuantificando el área del ciclo de histéresis y también, ajustando la variación del esfuerzo de cizalla con el tiempo al aplicar una velocidad de cizalla constante de 100 s^{-1}, a dos modelos: el modelo empírico de Weltmann ($\sigma=A-B\cdot\ln t$) y a un modelo de cinética estructural de segundo orden ($[(\eta_0-\eta_e)/(\eta-\eta_e)] = kt+1$). Las curvas de flujo obtenidas tras eliminar la dependencia del tiempo mediante cizallamiento se ajustaron bien al modelo de Herschel-Bulkley ($\sigma=\sigma_0+K\cdot\dot{\gamma}^n$). Se observaron diferencias significativas en el comportamiento de flujo de las muestras analizadas y en general, al aumentar la temperatura de medida de las muestras de natillas (de 5 a 25ºC), la dependencia del tiempo de su flujo, el umbral de fluencia y la consistencia disminuyeron y la pseudoplasticidad se incrementó ligeramente.

Las curvas de flujo obtenidas aplicando velocidades de cizalla menores, también indicaron un comportamiento pseudoplástico con una zona inicial de viscosidad newtoniana seguida de una zona en la que se registró una

disminución de la viscosidad aparente al aumentar la velocidad de cizalla. Los datos se ajustaron bien al modelo de Carreau simplificado ($\eta_{ap}=\eta_0/(1+(\dot{\gamma}/\dot{\gamma}_c)^2)^m$. Se observaron diferencias en los valores de los parámetros de dicho modelo para las distintas muestras. El cambio de la temperatura de medida influyó sobre todo en los valores de la viscosidad aparente en la zona newtoniana (η_0), que en todos los casos fueron inferiores cuando la medida se realizó a 25º C.

Con respecto a las propiedades viscoelásticas de las natillas comerciales, la mayoría presentó un espectro típico de gel débil con valores del módulo elástico (G') superiores a los del módulo viscoso (G'') y ligeramente dependientes de la frecuencia. No obstante, se observaron claras diferencias en los espectros de las muestras, tanto en los valores de los módulos como en la dependencia de la frecuencia. Especialmente, una de las muestras, cuyo espectro mecánico presentó valores de G' y G'' muy inferiores a los del resto y más dependientes de la frecuencia, exhibió un comportamiento más fluido, indicativo de una estructura más débil. Los valores de G' y de G'' obtenidos a 1Hz fueron menores a 25ºC que a 5ºC, pero su variación con la temperatura fue distinta para las diferentes muestras. Considerando la variación de los valores de la tangente del ángulo de desfase (tan δ) y de la viscosidad compleja ($\eta*$) a 1 Hz, se pudieron formar dos grupos de muestras en función de la variación de su viscoelasticidad con la temperatura de medida.

Las diferencias en consistencia perceptibles en las natillas de vainilla comerciales, se evaluaron con pruebas de ordenación, realizadas por un grupo de 42 catadores. Al analizar los datos con el análisis de la varianza de Friedman, se puso de manifiesto que existían diferencias significativas en su consistencia. Con objeto de analizar las posibles relaciones entre la variabilidad de los distintos parámetros reológicos y las variaciones en consistencia detectadas sensorialmente, se calcularon los valores del

coeficiente de correlación no parámetrico de Spearman (ρ). Las mejores correlaciones entre los datos sensoriales y los valores de los parámetros que caracterizan el flujo de las natillas fueron las obtenidas para el umbral de fluencia (ρ=0.96) y para la viscosidad aparente a 10 s^{-1} (ρ=0.89). Estos resultados coincidieron con los encontrados por otros autores en otros tipos de productos semisólidos. Aunque cuando se relacionaron los distintos parámetros viscoelásticos con la consistencia percibida, se obtuvieron unos valores significativos del coeficiente ρ con los valores de G" y de η∗ a 1 Hz, los valores de G' a 1Hz y los de η∗ a 50 $rad.s^{-1}$ fueron los que mejor se relacionaron con los datos sensoriales (ρ=0.92, en ambos casos). Este último parámetro, en concreto ya había sido considerado por otros autores como buen índice de la consistencia sensorial de productos semisólidos, con estructuras débilmente gelificada.

Con respecto al color, las natillas de vainilla comerciales presentaron un espectro similar, con valores máximos de reflexión en la región definida por valores de la longitud de onda (λ) que oscila entre 500 y 700 nm, característico de materiales con colores entre el amarillo y el rojo. Se detectaron diferencias significativas (α=0.05) en los valores de los parámetros instrumentales de color: *L** (luminosidad), *a** (componente rojo), *b** (componente amarillo), *C** (chroma) y *h** (hue) entre las distintas muestras. Las diferencias perceptibles en el color de las natillas de vainilla comerciales también se evaluaron sensorialmente detectándose diferencias significativas entre las muestras. Al estudiar la relación entre las medidas sensoriales e instrumentales del color, los parámetros colorimétricos que mejor se relacionaron con la evaluación sensorial fueron L*, a* y h* con valores del coeficiente de correlación de Sperman de -0.964, 0.893 y -0.964 respectivamente. Considerando conjuntamente los valores de estos tres parámetros, se pueden predecir las diferencias en color de las natillas detectadas sensorialmente.

En resumen, se observó una gran variabilidad tanto en el color como en la textura de las muestras de natillas comerciales. La variabilidad en el comportamiento reológico y en las medidas colorimétricas se tradujo en diferencias perceptibles en la consistencia y en el color en las muestras analizadas. Es evidente que la variabilidad detectada responde a diferencias en la composición de las natillas y en las condiciones del proceso de fabricación. Para poder establecer la influencia de los distintos ingredientes en las características físicas y sensoriales de estos productos, es necesario analizar el efecto de los mismos y de las interacciones entre ellos en las características del producto final.

2. Comportamiento reológico de las dispersiones de almidón en leche

Los ingredientes básicos de las natillas de vainilla son la leche, el almidón, ciertos hidrocoloides, el azúcar, aromas y colorantes. Sus propiedades reologicas y sensoriales dependen principalmente de las características particulares de algunos de estos ingredientes como el contenido en grasa de la leche, el tipo y la concentración del almidón y del hidrocoloide y de las posibles interacciones entre ellos.

En primer lugar, se estudiaron las diferencias en el comportamiento reológico de dispersiones de almidón nativo y de almidón modificado en leche. En concreto se estudiaron los efectos de la concentración de almidón y de la adición de λ-carragenato en los valores del umbral de fluencia. Para ambos tipos de almidón, al aumentar la concentración de almidón se incrementó el valor del umbral de fluencia, pero este incremento fue considerablemente menor en las dispersiones de almidón nativo en las que además, la estructura responsable del umbral de fluencia mostró ser muy sensible al cizallamiento. La adición de λ-carragenato produjo un considerable incremento de los valores del umbral de fluencia que se

atribuyó a la suma de dos efectos: al incremento de la concentración efectiva de almidón debida a la capacidad del carrageneato de inmovilizar agua y a la formación de una red carragenato-caseína favorecida por la presencia simultánea de carragenato y caseína en la fase continua del sistema. No obstante, la magnitud del efecto de la adición del λ-carragenato dependió en gran medida del tipo de almidón lo que indicó que el almidón juega uno de los papeles más importantes en la estructura y características de este tipo de sistemas (almidón-leche-carragenato).

Posteriormente, se seleccionaron tres tipos de almidón modificado de grado de entrecruzamiento similar y de uso habitual en la fabricación de postres lácteos y se estudió el comportamiento de flujo y la viscoelasticidad de las dispersiones elaboradas en agua y en leche con distintas concentraciones de los tres almidones. Todas las muestras tuvieron un comportamiento de flujo pseudoplástico con una cierta resistencia inicial a fluir y en la mayoría de los casos, dependiente del tiempo (tixotrópico o antitixotrópico). Los valores del umbral de fluencia y la viscosidad aparente se incrementaron al aumentar la concentración de almidón. La sustitución de leche por agua también produjo un incremento en los valores de ambos parámetros y la magnitud de este incremento fue diferente dependiendo de la concentración de almidón pero similar para los tres tipos de almidón. Se observó una gran variabilidad en las características viscoelásticas de las muestras que dependieron principalmente de la concentración de almidón y del tipo de medio dispersante (agua o leche). En general los valores de G' y G''a 1Hz se incrementaron con la concentración de almidón mientras que los valores de la tan δ disminuyeron indicando un incremento relativo de la contribución del componente elástico a la viscoelasticidad del sistema.

En resumen, el uso de almidón modificado permitió obtener dispersiones más resistentes a la agitación que el almidón nativo y tanto con el incremento de la concentración de almidón como con la adición de λ-

carragenato se obtuvieron dispersiones de mayor consistencia con el almidón modificado que con el almidón nativo. En cambio, las diferencias observadas entre los tres tipos de almidón modificado, tanto en el comportamiento reológico como en los efectos de la concentración de almidón y del medio dispersante en el mismo, aunque detectables, fueron de poca entidad.

3. Influencia de la composición y de la adición de inulina en el comportamiento reológico y en la textura y el sabor de sistemas modelo de natillas de vainilla

De acuerdo con la información obtenida en los estudios realizados en dispersiones lácteas de almidón, y en otros ensayos preliminares, se seleccionaron: un almidón modificado de maíz, un carragenato, enriquecido en la fracción λ y una inulina modificada, de alto grado de polimerización, para estudiar, en sistemas modelo de natillas de vainilla con cantidades fijas de azúcar, de aroma de vainilla y de colorante, la influencia de las variaciones de composición en sus características reológicas y sensoriales.

En primer lugar, se estudiaron los efectos de la concentración de almidón, de la concentración de λ-carragenato y del contenido en grasa de la leche y de las interacciones entre ellos, en la variación de la viscosidad aparente durante el proceso de elaboración, en la viscoelasticidad y en el sabor y en la textura de los productos finales. Al registrar la variación de la viscosidad aparente durante el proceso térmico de elaboración, se observó que tanto al incrementar la concentración de almidón como la de λ-carragenato, los valores de la viscosidad aparente aumentaron. Además, las muestras con concentraciones de λ-carragenato superiores a 0.06%, presentaron durante el enfriamiento un pronunciado pico y alcanzaron el valor máximo de viscosidad aparente antes (a temperatura más elevada) que las muestras sin

carragenato. Dependiendo de la composición de los distintos sistemas, se observó una gran variabilidad en los espectros mecánicos, tanto en los valores de los módulos como en la dependencia de éstos de la frecuencia. La mayoría de los sistemas presentaron un comportamiento típico de gel, excepto las muestras con concentraciones bajas de almidón y sin carragenato que presentaron un comportamiento más fluido. Al aumentar la concentración de almidón y de λ-carragenato, los valores de G' a 1 Hz se incrementaron. El efecto del contenido en grasa fue distinto dependiendo de la concentración de λ-carragenato, mientras que para concentraciones de carragenato inferiores a 0.1%, las muestras con leche entera presentaron valores de G' mayores que las de leche desnatada, para concentraciones superiores a 0.1%, el efecto fue el contrario.

Como cabría esperar, al aumentar la concentración de λ-carragenato se incrementó significativamente la consistencia perceptible, tanto en las muestras elaboradas con leche entera como en las elaboradas con leche desnatada. Sin embargo la variación en la cremosidad no evolucionó paralelamente a la de la consistencia. Al aumentar la concentración de carragenato hasta 0.06%, se incrementó la cremosidad de las muestras, pero a partir de esta concentración, el incremento de λ-carragenato, no produjo cambios significativos en la cremosidad de las muestras con leche desnatada e incluso, disminuyó la cremosidad en las muestras con leche entera. En general las muestras con mayor concentración de carragenato se percibieron como con menor sabor a vainilla y menos dulces, aunque las diferencias perceptibles entre ellas fueron distintas según el tipo de leche.

Posteriormente, se estudió el efecto de la adición del 6% de inulina en las propiedades reológicas y sensoriales de sistemas modelo de natillas de vainilla de bajo contenido en grasa y elaboradas con distintas concentraciones de almidón. La posible utilidad de la inulina como sustituto de grasa se estudió comparando sus características reológicas y sensoriales

con las de las muestras elaboradas con leche entera. La adición de inulina modificó el comportamiento de flujo y la viscoelasticidad de las muestras, tanto de las elaboradas con leche entera como de las elaboradas con leche desnatada. En general, las muestras de natillas con leche desnatada e inulina y las muestras con leche entera, mostraron un comportamiento reológico similar y significativamente diferente de las muestras con leche desnatada y sin inulina. Con respecto a las propiedades sensoriales, la adición de inulina en natillas con bajo contenido en grasa produjo un incremento del dulzor, de la consistencia y de la cremosidad de las muestras excepto para el caso de las muestras con mayor concentración de almidón en las que la cremosidad de las muestras elaboradas con o sin inulina no fue significativamente diferente. Las diferencias en las características sensoriales de las muestras elaboradas con leche desnatada e inulina y las muestras elaboradas con leche entera dependieron de la concentración de almidón. A bajas concentraciones de almidón no se detectaron diferencias en la consistencia ni en la cremosidad de las muestras pero a alta concentración de almidón, la muestras con leche entera se percibieron como más cremosas y más consistentes que la muestras con inulina.

En resumen, variando las concentraciones de almidón y de λ-carragenato y el contenido en grasa de la leche, se puede obtener un espectro de productos de diferentes características físicas y sensoriales. El aumento de la concentración de λ-carragenato y de almidón produjo un aumento de la elasticidad de las muestras, mientras que la disminución del contenido de grasa dio lugar a un aumento o a una disminución de la misma, dependiendo de la concentración de carragenato y de almidón. Aumentando la concentración de carragenato hasta 0.06% se incrementó la cremosidad de las muestras pero las muestras con mayor concentración de carragenato se percibieron con menor sabor a vainilla y menos dulces. La adición de un 6% de inulina en sistemas modelo de natillas con bajo contenido en grasa

produjo, en general, un aumento de la consistencia, de la cremosidad y del dulzor, aunque estos efectos dependieron de la concentración de almidón.

La información obtenida en esta tesis abre nuevas expectativas para el diseño y optimización de nuevos productos de postres lácteos bajos en grasa o con propiedades nutritivas especiales y que satisfagan los requerimientos de distintos sectores de la población.

CONCLUSIONES

Del estudio realizado sobre la influencia de la composición en las propiedades físicas y sensoriales de postres lácteos, se pueden establecer las siguientes conclusiones generales:

1. Existe una variabilidad importante en el comportamiento reológico y en el color, medido instrumentalmente, de las natillas comerciales de vainilla y esta variabilidad se traduce en diferencias significativas en la textura y en el color percibidos sensorialmente en estos productos.

2. Los valores del umbral de fluencia, de la viscosidad aparente a $10s^{-1}$, del módulo elástico a 1Hz y de la viscosidad compleja a 50 $rad.s^{-1}$ pueden ser utilizados como índices instrumentales de la consistencia sensorial y la consideración conjunta de los valores de L^* (luminosidad), a^* (componente rojo) y h^* (hue) permite predecir las diferencias en color de las natillas percibidas sensorialmente.

3. Los almidones modificados de grado de entrecruzamiento medio, de maíz y de tapioca son adecuados para la fabricación de postres lácteos gelificados. La utilización de carragenato enriquecido en la fracción λ, en concentraciones inferiores a 0.06%, permite obtener natillas de una consistencia adecuada e incrementa su cremosidad tanto si se elaboran con leche entera como si se utiliza leche desnatada aunque reduce ligeramente la intensidad del sabor a vainilla y el dulzor.

4. La adición de inulina de alto grado de polimerización a una concentración del 6% a natillas elaboradas con leche desnatada, además de dar lugar a un producto enriquecido en fibra y con

carácter prebiótico, incrementa significativamente la consistencia, el dulzor y la cremosidad y no modifica la intensidad del sabor a vainilla del producto aunque estos efectos dependen de la concentración de almidón utilizada.

5. La información obtenida constituye una base imprescindible para abordar el diseño y optimización de una nueva gama de productos funcionales lácteos.